Investigating manganese reduction pathways in groundwater sand filters

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Abstract

Conventional groundwater treatment plants consist of aeration and rapid sand filtration steps, that are merely designed and optimized for iron (Fe), manganese (Mn) and ammonium (NH_4^+) removal. Understanding the various reduction-oxidation pathways, and interactions of manganese and iron, can play a major role in optimizing the performance of such filters. Interestingly, it is found that under certain conditions, mobilization of dissolved manganese can occur in such filters, which can be critical to the filter operation. Therefore, the main aim of this research is to dive deep into studying the possibilities of manganese reduction pathways occurring at the top layer of the filter media of a groundwater filter. Secondly, the research also focuses on knowing how the removal of manganese is related to the oxidation by MnO_2+O_2 systems, and also how these systems interact with each other under different pH conditions.

To do so, manganese dioxide (MnO_2) coated sand grains were obtained from the second filtration unit of Vitens groundwater treatment plant situated in Holten. Various batch scale experiments were done under aerobic as well as anoxic conditions, in the presence of Mn(II) or Fe(II). Additionally, the influence of pH on manganese removal efficiencies as well as the rates of both manganese and iron oxidation was investigated.

It was found that the dissolved Mn was a reduction product of MnO_2-Fe(II) system, where Mn(IV) got reduced to Mn(II), reaching an Fe(II) : Mn(II) molar ratio of 3.65:1 instead of 2:1, as there was a significant difference between the calculated theoretical values and the measured experimental values of both Mn(II) and Fe(II). There was mobilization of Mn(II) which took place from the MnO_2 surface, when there was a presence of Fe(II) in the system, which simultaneously got partially oxidized to Fe(III). Also, it was observed that manganese could be removed by MnO_2 under anoxic conditions, although under aerobic conditions the removal efficiency was high (93.32% vs 71.83%). Apart from oxidation, there is a possibility of adsorption over MnO_2 due to its high sorption capacity towards cations like Mn^{2+}, Mn^{3+} and Fe^{2+}. This research also showed that a small fraction of Mn(II) reacts with Mn(IV) to form Mn(III) as a reaction product, enhancing the mobilization of Mn(II).

Nomenclature

List of Acronyms

Fe	Iron
Mn	Manganese
NH_4^+	Ammonium
MnO_2	Manganese dioxide
MnO_x	Manganese oxide
δMnO_2	Delta Manganese oxide
Fe(II)	Ferrous iron
Fe(III)	Ferric iron
Mn(II)	Manganese(2+)ion
Mn(III)	Manganese(3+)ion
Mn(IV)	Manganese(4+)ion
$Mn_{(aq)}^{2+}$	Aqueous Mn(2+)ion
MOCS	Manganese Oxide-Coated Sand(MOCS)
MOCA	Manganese Oxide-Coated Anthracite
$Mn(H_2O)_2^{6+}$	Hexaquamanganese(II)
MnO_4^-	Permanganate
FeOOH	Iron(III) oxide-hydroxide
Fe_2O_3	Iron(III) oxide
ClO_2	Chlorine dioxide
O_3	Ozone

PO_4^{3-}	Phosphate ion
DO	Dissolved oxygen
HFO	Hydrous Ferric Oxide
ORP	Oxidation-reduction Potential
XAS	X-ray absorption spectroscopy
XRD	X-Ray Diffraction
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
NH_4Cl	Ammonium Chloride
NaH_2PO_4	Monosodium Phosphate
$NaHCO_3$	Bicarbonate of Soda
NaOH	Sodium hydroxide
H_2SO_4	Sulphuric acid
rpm	Revolutions per minute

Contents

1) Introduction

1.1) Theoretical Background

Groundwater is one of the most important sources of drinking water production in the world (UNEP, 2002). However, groundwater is often contaminated by inorganic pollutants like iron, manganese and ammonium. Just like iron and ammonium, manganese is a commonly occurring contaminant present in most groundwater (WHO, 2004). Manganese can exist in multiple oxidation states, but the most abundant and stable manganese species available in anaerobic groundwater is Mn^{2+} (low pH and redox potential) (Stumm and Morgan, 1996). It causes aesthetic, organoleptic and operating problems that not only affects the water quality, but also induces corrosion in distribution networks, generating operational and system maintenance problems (Piazza et al., 2019).

There exists various manganese removal mechanisms, and some of the main ones are:

i) Physico-chemical processes like adsorption and oxidation
ii) Co-precipitation
iii) Manganese oxidation and removal by micro-organisms
iv) Or a combination of all these processes (Bruins, 2016)

Chemically, the dissolved Mn(II), a divalent cation, is oxidized to particulate Mn(IV) and then physically these solids can be separated from the solution through clarification, filtration and precipitation processes (Tobiason et al., 2016). It can also be removed by sorption to a solid surface, typically a metal oxide, and most often a manganese oxide, in the pH range of 6 to 9 (Knocke et al., 1988). Processes like co-precipitation also helps in manganese removal by formation of Mn-Fe co-oxides via simultaneous precipitation. Thirdly, micro-organisms also support in manganese removal by oxidizing it via direct intra-cellular oxidation, extracellular adsorption or catalysis of Mn(II) oxidation by biopolymers generated from microorganisms (Tobiason et al., 2016).

The most conventional manganese removal process is aeration followed by rapid sand filtration, when it comes to manganese (Mn) removal in groundwater sand filters (Gude et al., 2017). In groundwater treatment plants, during aeration, Fe(II) is oxidized and sorbed on the formed iron oxides but remains in suspension until it is removed during the subsequent biological filtration stage. NH_4^+ is biologically oxidized and removed from the water via nitrification and formation of nitrates. In addition to naturally occurring compounds, such as Fe(II) and NH^{4+}, groundwater frequently contains dissolved manganese in excess of drinking water standards (Katsoyiannis et al. 2008). During the production of drinking water by means of rapid sand filtration, soluble Mn(II) is commonly removed through oxidation and precipitation of the insoluble Mn-oxides in a filter bed (Vandenabeele et al.,1992). Mn(II) is oxidized by both biological oxidation as well as autocatalysis, and the produced insoluble manganese oxides are removed by filtration (Katsoyiannis et al. 2008). Hence, the basic idea to easily remove Fe(II) and Mn(II) is to aerate the oxygen-free groundwater and convert them to oxides and hydroxides, respectively by passing them into rapid sand filters and hence, undergoing precipitation (Figure 1.1).

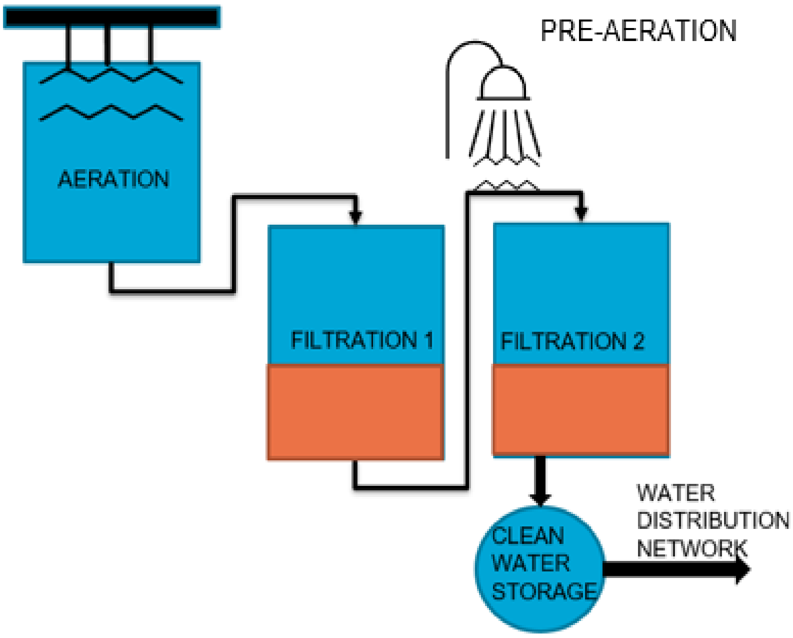


Figure 1.1: Schematic representation of a treatment scheme similar to the drinking water treatment plant of Vitens, Holten

In the Netherlands and Belgium, Mn removal is also commonly achieved with conventional aeration-filtration treatment, called contact filtration (Bruins et al., 2015). Also, under common groundwater conditions (e.g., low pH), manganese removal may be initiated by bacterial activity during aeration and filtration (Diem & Stumm 1984; Burger et al. 2008). Although, there are various benefits of aeration and rapid sand filtration, apart from being economically attractive, few of them are: (i) no chemicals required, (ii) dense possibly valuable, iron (Fe) rich waste streams are generated and (iii) biologically stable drinking water is produced (Gude et al., 2017).

However, aeration-filtration being efficient and cost effective, in practice it is frequently associated with a number of drawbacks such as: (i) very long ripening times of virgin filter media; several weeks to more than a year are required to achieve an efficient manganese removal (Cools 2010; Krull 2010), (ii) occasional manganese breakthrough of filters may occur after some years of operation, requiring filter media replacement, associated with additional costs for filter media disposal and replacement (Buamah et al. 2009a). Also, these aeration and filtration units in a typical groundwater treatment plant are merely optimized or designed for removal of these inorganic pollutants (Gude et al., 2017).

1.2) Full scale Manganese removal in groundwater sand filters

The efficient manganese removal in a filter with virgin sand is not achieved until after almost one year, however, it can take 1 to 4 months. Many authors (Hu et al. 2004a; Kim & Jung 2008; Kim et al. 2009) describe the potential of Manganese Oxide-Coated Sand (MOCS) to adsorb dissolved manganese from groundwater. It was also reported that removal of Mn^{2+} in filters with anthracite is enhanced by development of ‘catalytic oxide layers’ on aged anthracite, due to formation of Manganese Oxide-Coated Anthracite (MOCA) (Sahabi et al. 2009). (Buamah et al. 2008) also suggested that the performance of conventional manganese removal plants could be improved by introducing manganese and/or iron (hydro)oxide-rich filter media into rapid sand filters. When manganese oxide coated filter media are applied in water treatment, soluble manganese and iron oxidize on the grains of the media and very low manganese and iron concentrations are achieved as a result (Knocke et al., 1988).

In rapid sand filtration systems, Mn(II) removal is enhanced by the autocatalysis of MnO_x coated on the filter media—a process that is called contact catalytic oxidation. This autocatalysis is a two-step process: physicochemical autocatalytic adsorption and the subsequent oxidation of adsorbed Mn(II) (Eqs. (1) and (2)) (Stoerzinger et al., 2015); (Sahabi et al.,2009):

$$Mn(II) + MnO_x .yH_2O \rightarrow MnO_x .MnO_x.MnO(y-1)H_2O+2H^+ \qquad (1)$$

$$MnO_x .MnO_x.MnO(y-1)H_2O + (x\text{-}1)/2O_2 + H_2O \rightarrow 2MnO_x + yH_2O \qquad (2)$$

The oxidation kinetics of Mn(II) by dissolved oxygen (DO) in an aqueous solution can be expressed using equations (3)–(5) (Bruins et al.,2015; Diem and Stumm, 1984):

$$\frac{-d[\mathrm{Mn(II)}]}{dt} = -k_0[\mathrm{Mn(II)}]+(-k1)[\mathrm{Mn(II)}][\mathrm{MnO_X}] \quad (3)$$

$$k_0=K_1{}^{'}[O_2.aq][OH^-]^2 \quad (4)$$

$$k_1=K_2{}^{'}[O_2.aq][OH^-]^2 \quad (5)$$

From equations (4) and (5), it is observed that the reaction rate constant is greatly influenced by the DO and OH^- concentrations. High pH and high DO are considered optimal process conditions for Mn removal. Also, from equation (3), it can be configured that an increased manganese oxide concentration enhances the manganese removal. Mostly, it is indirectly by increasing the number of adsorption sites (Knocke et al., 1988). Whether it is the traditional contact catalytic oxidation technology or the biological oxidation technology, DO is a necessary and important factor for the removal of Mn. In groundwater treatment, aeration is often required because of the low DO levels in groundwater.

Additionally, research from (Zhang et al., 2002) showed how the dissolved oxygen concentrations effected the Mn oxidation rates at temperature = 25°C, pH = 7.5 and DO = 8.05 mg/L (Figure 1.2). Hence, it is evident that with high DO, more is the Mn oxidation, hence, better the Mn removal.

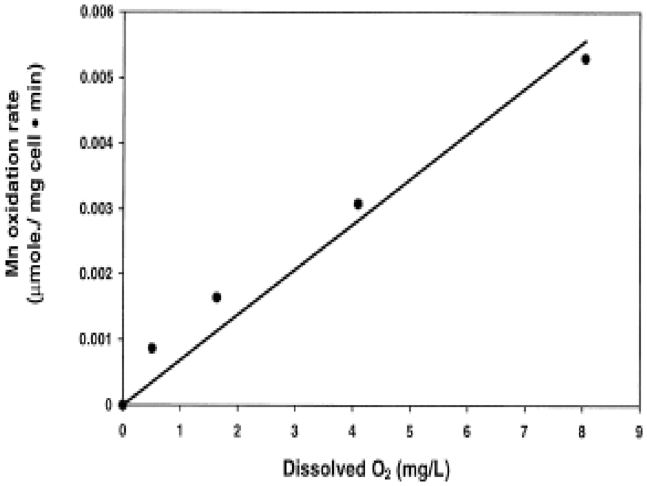


Figure 1.2: Effect of dissolved oxygen concentration on Mn oxidation rate in an experimental setup by (Zhang et al., 2002) at (A) T = 25°C, and O_2 = 8.05 mg/L and (B) T = 25°C, pH = 7.5 and O_2 = 8.05 mg/L

Also from the research of (Buamah, 2009), it is observed that the solubiliy of Mn(II) decreases with an increase in pH at a particular bicarbonate (HCO_3^-) concentration (Figure 1.3), thus, supporting the fact that it helps in forming insoluble precipitates for better manganese removal.

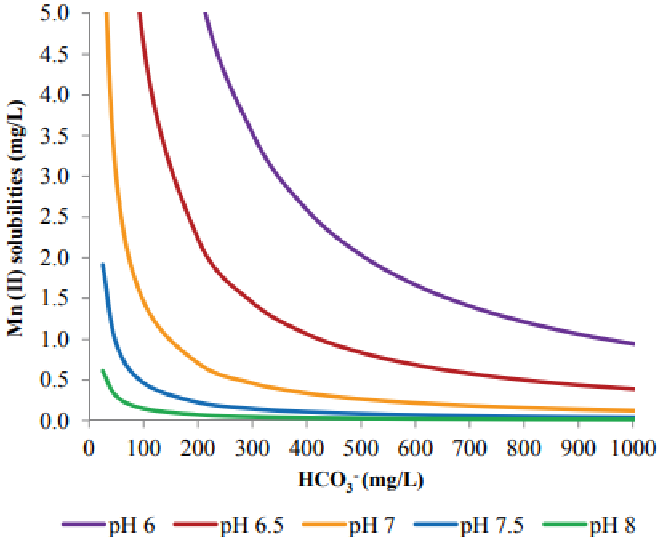


Figure 1.3: Solubility of Manganese (Mn(II)) as a function of pH and HCO3- concentration (Buamah, 2009)

(Cheng et al., 2017) reported that Mn oxidation states cycled in oxidation states of Mn(II), Mn(III) and Mn(IV) on MnOx, and played a critical role during catalytic oxidation of Mn(II) into Mn(IV). Also, MnOx continually coated onto the sand surface acted as catalysts for the adsorption and catalytic oxidation of Mn (Guo et al., 2017). It was further investigated that the active ingredients in this catalyst were MnOx, specifically hexagonal birnessite (Cheng et al., 2017) and adding strong oxidants may generate pre-coatings of MnOx onto the surface of the filter (Yang et al., 2020). Since, these Mn-oxide surfaces used for Mn removal have manganese in the Mn(III) or Mn(IV) oxidation state, or both, they are often referred to as “MnO_x(s)” with *x* between 1.5 and 2.0.

1.3) Manganese reduction

Groundwater also contains Fe(II) which gets oxidized to Fe(III) with a coupled complete reduction of Mn(IV) to Mn(II) (Schaefer et al.,2017) (Figure 1.4). Using X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) among other techniques, (Lafferty et al. 2010) showed increased Mn(III) content in a MnO_2 mineral as a result of Mn(II) sorption. Here, in our study, we primarily focused on the reduction pathways of Mn(IV). An interesting point is also the existence of Mn(III) metastable forms, which can be stable in certain minerals (Elzinga,2011) and is also described by the following equation:

$$2Mn(IV)O_2 + H_2O \rightarrow 2Mn(III)OOH + 0.5O_2 \qquad (6)$$

However, extensive experience has demonstrated that continuous abiotic oxidation of adsorbed Mn(II) by oxygen alone does not occur at typical drinking water conditions to an extent that effective treatment is achieved. In contrast, if reducing conditions develop in MnO_x-coated filter media, Mn release can occur from the reduction of MnO_x to Mn(II) (Tobiason et al., 2016).

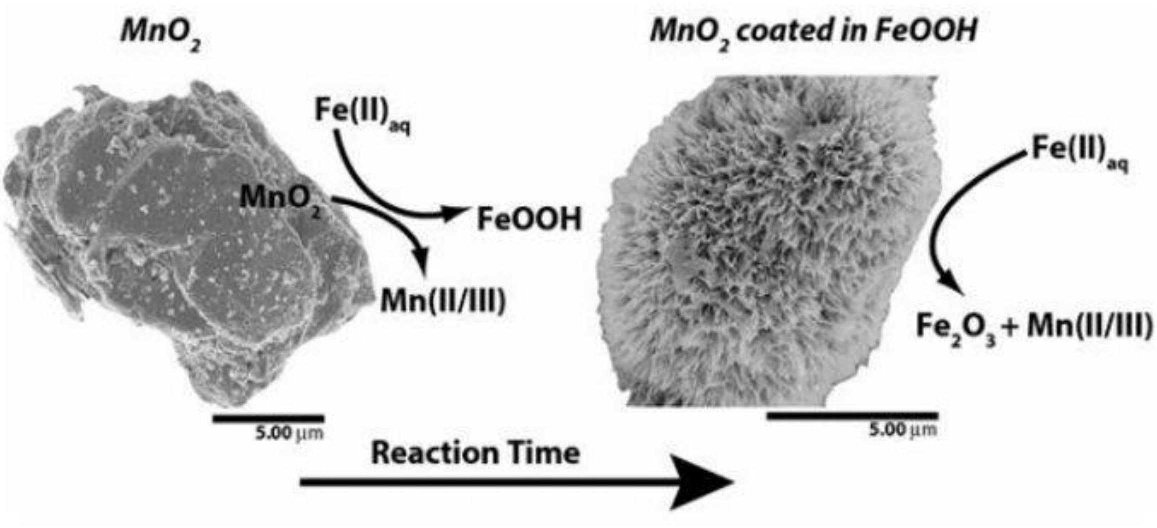


Figure 1.4: Manganese and iron redox interactions (Schaefer et al., 2017).

1.3) Research Framework

In order to better understand the mechanisms involved in groundwater sand filters, a deep study of the various manganese removal and reduction mechanisms has been done. Hence, this research gives us not only an insight to the manganese removal efficacies, but also to know how possible manganese reduction may occur in sand filters in order to optimize the functioning of such filters for the overall manganese removal.

1.3.1) Research Objective

The primary objective of this research is to investigate the possibility of manganese reduction in sand filters. Hence, finding out the conditions stimulating the mobilization of Mn(II) from filter grains is the main research goal. The scope of this research therefore lies in studying how these parameters influence the manganese reduction as well as removal processes and also to compare the rates quantitatively. The final goal is be to find out the possible manganese reduction pathways.

1.3.2) Research Questions

Based on the objectives, the research questions mentioned below follow up:

1. *"Is there any Mn(IV) reduction occurring in groundwater sand filters?"*
2. *"Under what conditions Mn(II) mobilization takes place?"*
3. *"What are the manganese reduction pathways in groundwater sand filters?*

Therefore, it can be hypothesized that depending on varying conditions of O_2, pH, and the presence or absence of Fe(II), MnO_2 gets reduced leading to the mobilization of Mn(II), as shown in (Figure 1.5). Lower the pH and DO, better will be the chances for manganese to follow a reduction pathway, and how to find this out is briefly described in the following materials and methods section.

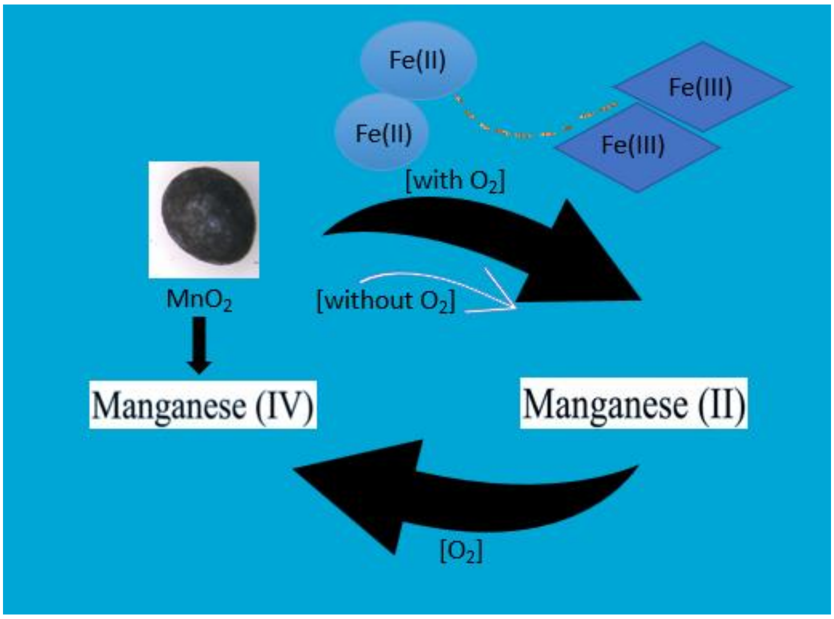


Figure 1.5 : Possible manganese redox pathways based on presence and absence of Mn(II)/Fe(II)/O_2

2) Materials and Methods

Simple batch experiments were performed to study the dissolved Mn & Fe concentrations with both commercial MnO_x material and MnO_2 filter media extracted from the second filter of Vitens, Holten (Figure 1). The MnO_2 filter media was extracted from the second filter of Vitens, Holten because there has been years and years of manganese removal occurring in this unit, which eventually formed a fresh coating of MnO_2 over the filter media, as most of the iron and ammonium got already oxidized in the first filter. Batch experiments were performed in oxygenated and anoxic conditions, with buffered demineralized water at pH=6.5, 7.5 and 8.5. The possibility of the mobilization of Mn(II) in an MnO_2+Fe(II) system and removal of Mn(II) in an MnO_2+Mn(II) system is studied and compared to find out all possible manganese redox pathways. Most of the experimental procedures were followed from the paper of (Gude et al., 2017).

A schematic representation and an image of the lab setup for the preliminary batch studies is shown (Figure 2.1). It consists of a glass jar (Schott Duran Glass of 500 ml) into which 250 ml of demineralized water along with 1.47 ml of 2.95 millimolar $NaHCO_3$ solution, 130µL of 0.016 millimolar NaH_2PO_4 solution and 100µL of 0.036 millimolar NH_4Cl solution, as a buffer, was poured for all experiments. 10g wet weight of the synthetic MnO_X material was dosed in each of the experiments to perform these preliminary studies. The initial pH of the water solution was maintained between 7.4-7.6 by pH adjustments using 1M NaOH and 0.1M H_2SO_4 using droppers. A pH and a DO meter was used to monitor a circumneutral pH and a DO of about 10mg/L throughout the experiment to maintain conditions similar to a typical groundwater filter. The entire setup was rotated at speed 110 rpm by an orbital shaker to properly mix the water solution. The experiment duration was 120 mins with sampling times were set at t=0, 5, 10, 15, 20, 30, 45, 60, 90 and 120 mins.

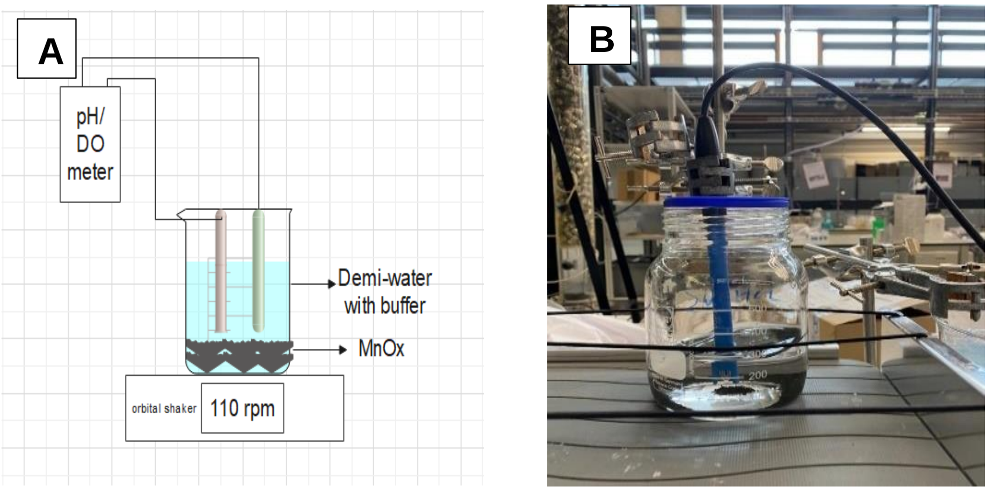


Figure 2.1: Schematic diagram (A) and experimental setup (B) of the preliminary batch reactor

Initially, in order to test the new experimental setup, triplicate batch experiments were performed with only the commercial MnO_x material (Aquamandix), starting with a set of control experiments, followed by experiments dosing 1mg/L of dissolved Mn, or 1mg/L of dissolved Fe, or 1mg/L of dissolved Mn and 1mg/L of dissolved Fe together (Appendix 37). Later few experiments were performed by decreasing the MnO_X wet weight to 5g and also increasing the dissolved Fe dosed to 10mg/L to well differentiate the redox processes in the system, since our initial target was to play with concentrations available inside a typical groundwater filter. The ammonium concentration in the buffer was 0.5 mg N/L. The pH was maintained between 7.4-7.6 and the DO about 9-10mg/L. An overall experimental overview is shown in (Appendix 37).

The next improved experimental setup was similar to (Figure 2.1), except this time we used a glass jar (Simax Czech Republic Retrace Cool Glass of 500 ml) and covered it up with a parafilm sheet, as shown in (Figure 2.2). To make the setup completely anoxic, we dosed N_2 gas directly into the beaker filled with 250 ml of demineralized water and 1.47 ml of 2.95 millimolar $NaHCO_3$ solution with 130µL of 0.016 millimolar NaH_2PO_4 solution, which was also rotated at speed 110 rpm by the orbital shaker. The NH_4Cl solution was not dosed this time to reduce the complexity of the initial water solution. Also this time a scoop of 5g wet weight of the MnO_2 granules, extracted from the filter media of Vitens, Holten was used in each of the experiments. The initial pH of the water solution was maintained between 7.4-7.6 by pH adjustments using 1M NaOH and 0.1M H_2SO_4. A pH and a DO meter was used to monitor a circumneutral pH and a DO of 0.0-0.03 mg/L throughout the experiment. The experiment duration was reduced to 30 mins with sampling times at t=0, 1, 5, 10, 15 and 30 mins.

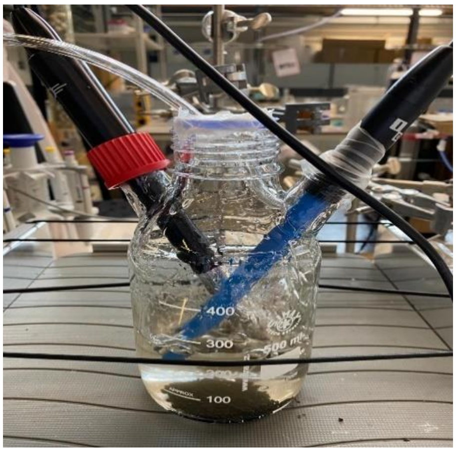


Figure 2.2: Experimental setup of the anoxic batch reactor

These jar experiments were also performed in triplicates, also consisted of a set of control experiments done with only the extracted filter media (MnO_2), followed by experiments dosing 1mg/L of dissolved Mn, or 10mg/L of dissolved Fe. Few experiments were performed by just adding 1mg/L of dissolved Mn, or 10mg/L of dissolved Fe separately, with only the water solution, without adding any MnO_2 grains (control). The wet weight for these MnO_2 filter media when used, was 5g. The pH was maintained between 7.4-7.6 and the DO about 0.0-0.03 mg/L. Table 2.1 shows the overall operational parameters of these experiments.

Table 2.1 Operational parameters for anoxic jar experiments

Experiment	MnO2, Vitens	Dissolved Mn	Dissolved Fe
Control	20 g/L	-	-
Mn+MnO_2	20 g/L	1 mg/L	-
Mn	-	1 mg/L	-
Fe+MnO_2	20 g/L	-	10 mg/L
Fe	-	-	10 mg/L

Similar setups of Fig 2.1 & Fig. 2.2 were used, former as an aerobic setup and the latter one as anoxic. The experimental conditions were exactly same as described before, and the MnO_2 filter media from Vitens was used again. This time the experiments were performed at different pH, that is, 6.5, 7.5 and 8.5. The experiment duration was further reduced to 10 mins with sampling times at t=0, 1, 5, 10 mins to study the very initial behaviour of Mn & Fe.

2.1) Full scale Mn removal in the filter of WTP Holten

After several years of the operation of the filters at the water treatment plant of Vitens, Holten, a coating of MnO_2 has been formed over the filter media consisting of Quartz. This is due to the continuous removal of manganese in the form of conversion into manganese oxides that get trapped on the outer layer of the filter media. Since, most of the manganese is removed from the second filter unit (NAF1 filter), samples of the filter media was scooped up using a 30cm sampling equipment which appear to look shiny grey (Figure 2.3). Sampling was done From the top 30cm, 30-50cm and below 50cm filter depth. The grains vary in size about 200µm to 3500µm of width and are mostly irregularly spherical in nature. Before undergoing microscopic analysis, the filter media was properly rinsed in a 1000ml beaker consisting of demineralized water until all the sand deposits on the top of the filter media was decanted out of the solution. It was proceeded by overnight drying at 35°C and analyzed in the microscope the next day to better understand the morphology.

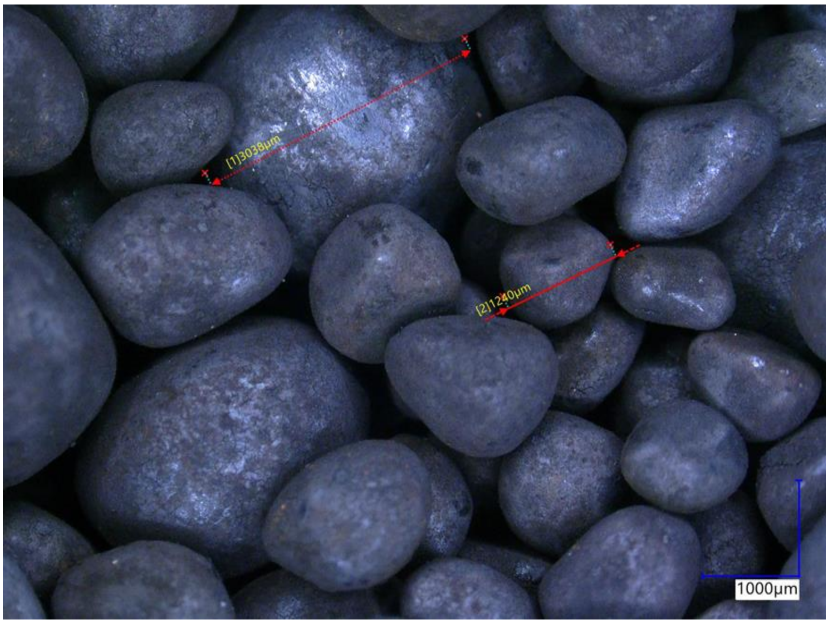


Figure 2.3: Microscopic image of the second filter media from Vitens, Holten

Following is a representation of the groundwater matrix of the plant (Table 2.2). It shows pH data and the concentrations of Mn, Fe, NH_4, etc. of the groundwater influent in mg/L. The pH is about 5.99 and the initial concentrations of the total Mn is 0.977, NH_4 is 0.15 mg/L, and Fe is 7.59mg/L.

Table 2.2 Groundwater matrix

NO_2	mg NO_2/l	<0.01
Mg	mg/l	6.26
pH	pH	5.99
Ca	mg/l	23.5
NH_4	mg NH_4/l	0.15
NO_2-N	mg N/l	<0.003
P	mg P/l	0.03
NH_4-N	mg N/l	0.12
NO_3-N	mg N/l	4.28
Fe	mg/l	7.59
NO_3	mg NO_3/l	19.0
Mn	mg/l	0.977
PO_4	mg PO_4/l	0.09

3.2) MnO_2 reduction by Mn(II)

The first experimental aim was the investigation of possible MnO_2 reduction or Mn(II) removal efficiencies in an MnO_2-Mn(II) system under various DO and pH conditions. As mentioned above, triplicate experiments were performed by dosing 1mg/L of dissolved manganese (Mn(II)) consisting of beakers with 250mL of the original buffered stock solution, also containing 5g wet weight of MnO_2 filter media. Similarly, few experiments were again performed by just adding 1mg/L of dissolved Mn only with the original buffered stock solution, without adding any MnO_2 grains, and is termed as control experiments. These experiments were performed both at anoxic and aerobic conditions to see the behaviour of manganese removal in both the situations. For the anoxic experiments, there was N_2 dosage, the setup being covered by parafilm sheet, whereas, for the aerobic ones, the lid was just open and the water solution was exposed to the atmospheric O_2. The DO was maintained around 9-10 mg/L for the aerobic setup and 0.0-0.03 mg/L for the anoxic. The wet weight for these MnO_2 filter media was maintained the same. Analysis of all these experiments were done after sampling at different time intervals, either by ICP-MS or HACH kits. Hence, in this manner the effect of both DO and pH in the MnO_2 reduction was studied. Table 2.3 shows the overall operational parameters of these experiments.

Table 2.3 Operational parameters for jar experiments with dissolved Mn at varying pH & Oxic/Anoxic conditions

Experiment	**MnO_2**	**Dissolved Mn**	**O_2/N_2**	**pH**
Control (oxic)	5g	-	O_2	6.5
Control (oxic)	5g	-	O_2	7.5
Control (oxic)	5g	-	O_2	8.5
Control (anoxic)	5g	-	N_2	6.5
Control (anoxic)	5g	-	N_2	7.5
Control (anoxic)	5g	-	N_2	8.5
Mn+MnO_2 (oxic)	5g	1 mg/L	O_2	6.5
Mn+MnO_2 (oxic)	5g	1 mg/L	O_2	7.5
Mn+MnO_2 (oxic)	5g	1 mg/L	O_2	8.5
Mn+MnO_2 (anoxic)	5g	1 mg/L	N_2	6.5
Mn+MnO_2 (anoxic)	5g	1 mg/L	N_2	7.5
Mn+MnO_2 (anoxic)	5g	1 mg/L	N_2	8.5

Equations (1) and (2) from section 1.2, defines the autocatalytic manganese removal mechanisms and equations (3), (4) and (5) shows how it is effected by both DO and pH. Hence, as the reaction rate constant is greatly influenced by the DO and OH^- concentrations, in order to understand it intricately, experiments with an MnO_2-Mn(II) system are performed.

3.2) MnO_2 reduction by Fe(II)

The second aim was to find out possible MnO_2 reduction or Fe(II), in an MnO_2-Mn(II) system under various DO and pH conditions. As hypothesized before, there is a possibility of manganese mobilization or release when Fe(II) reacts with MnO_2 and is shown by equation(6), and to check which parameters really effect this manganese mobilization and how, these experiments were performed. Once again triplicate experiments were performed by dosing 10mg/L of dissolved iron (Fe(II)) consisting of beakers with 250mL of the original buffered stock solution, also containing 5g wet weight of MnO_2 filter media. Control experiments were also performed by just adding 10mg/L of dissolved Fe only with the original buffered stock solution, without adding any MnO_2 grains. These experiments were also performed both at anoxic and aerobic conditions to see the behaviour of possible MnO_2 reduction in both the situations as mentioned in the previous section. The DO was maintained around 9-10 mg/L for the aerobic setup and 0.0-0.03 mg/L for the anoxic and the wet weight for these MnO_2 filter media was maintained the same. The analysis of all these experiments were also done by ICP-MS or HACH kits. The overall operational parameters for these experiments is shown in Table 2.4.

From literature it is found that Fe(II) in the groundwater can also react on the MnO_2 mineral surface, resulting in formation of Hydrous Ferric Oxides (HFO) and mobilization of Mn(II) (Postma, 1985; Postma and Appelo, 2000), shown by equation (7) as:

$$2Fe^{2+} + MnO_2 + 2H_2O \rightarrow 2FeOOH + Mn^{2+} + 2H^+ \qquad (7)$$

Hence, from the above equation it can be said that there is simultaneous reduction of Mn(IV) to Mn(II) and oxidation of Fe(II) to Fe(III), but in order to investigate which parameters of the DO and pH influence all these redox interactions, experiments with an MnO_2-Fe(II) system are performed.

Table 2.4 Operational parameters for jar experiments with dissolved Fe at varying pH & Oxic/Anoxic conditions

Experiment	MnO_2	Dissolved Fe	O_2/N_2	pH
Control with Fe (oxic)	-	10 mg/L	O_2	6.5
Control with Fe (oxic)	-	10 mg/L	O_2	7.5
Control with Fe (oxic)	-	10 mg/L	O_2	8.5
Control with Fe (anoxic)	-	10 mg/L	N_2	6.5
Control with Fe (anoxic)	-	10 mg/L	N_2	7.5
Control with Fe (anoxic)	-	10 mg/L	N_2	8.5
Fe+MnO_2 (oxic)	5g	10 mg/L	O_2	6.5
Fe+MnO_2 (oxic)	5g	10 mg/L	O_2	7.5
Fe+MnO_2 (oxic)	5g	10 mg/L	O_2	8.5
Fe+MnO_2 (anoxic)	5g	10 mg/L	N_2	6.5
Fe+MnO_2 (anoxic)	5g	10 mg/L	N_2	7.5
Fe+MnO_2 (anoxic)	5g	10 mg/L	N_2	8.5

There were several chemicals used in these batch experiments. The stock solution was always freshly prepared with 250ml demineralized water collected from the dm-tap of the green lab, with 1.47 ml of 2.95 millimolar $NaHCO_3$ solution and 130µL of 0.016 millimolar NaH_2PO_4 solution (purchased from Sigma-Aldrich, purity>99%) as a buffer. The 100µL of 0.036 millimolar NH_4Cl solution (Sigma-Aldrich, purity>99%) was used for the preliminary experiments to check if the NH_4 oxidation can be studied after the experiments. The stock solution of dissolved Fe, that is about 1ml of 10 mg Fe/L was prepared from the compound $FeCl_2(4)H_2O$ (purity>99%, Sigma-Aldrich). Similarly, the stock solution of dissolved Mn, that is about 101µL of 1mg Mn/L was prepared from the compound $MnCl_2(4)H_2O$ (purity>99%, Sigma-Aldrich). Also, while performing experiments with dissolved Fe, a 100µL of 1M H_2SO_4 (Merck Millipore) was added to the sample tubes, in order to acidify and control the fast reaction inside the tubes. The N_2 was dosed to the experimental jars to create an anoxic condition, at a pressure of about 1.5-2 atm, attached to a cylinder.

Samples were also collected from the filter at different heights by properly monitoring the DO and temperature at the time of sampling. Samples were immediately filtered and acidified at site according to the requirement of each experiment. After preparation of the samples in 15ml vials, ICP-MS analysis was done to find the total and the dissolved manganese, iron and ammonium measurements. About 2ml of samples were collected in 15 mL sample vials, once by filtering with a 0.20µm polysthersulfone filter (Macherey-Nagel GmbH & Co.KG) and the other one unfiltered at each time interval. 5ml syringe tubes were used for sampling the filtered samples. The filtered one was to determine the dissolved Fe & Mn concentrations and the unfiltered one was to determine the total Fe & Mn concentrations. The sampling time started after the dissolved Mn or Fe was first dosed into the water solution, mixed immediately and the pH was brought to the desired level by dosing 0.1 M H_2SO_4 acid or 1M NaOH base. Pre-acidification was done while performing the experiments involving dissolved Fe by adding 100µL of 1M H_2SO_4 (Merck Millipore) into the sample tubes. The sampling process was done by pipetting out the 2ml samples from the reacting jar by the use of the pipettes with the range of 1-5ml. For the acidification of samples and for the dosing of dissolved Mn and Fe, the pipette with the range of 100µL-1000µL was used. The samples were then kept inside the refrigerator at 4°C and acidified with ultrapure nitric acid (HNO_3 Ultra quality, ROTIPURAN$^{®}$ Ultra 69%) to dissolve any particles present in the sample and to preserve it.

The difference between the total Fe concentration and the dissolved Fe(II) concentration gave the values of Fe(III) concentrations. For Mn it can’t be surely said that the difference of total Mn concentration and the dissolved Mn(II) concentration will give the values of Mn(III) concentrations necessarily. These total and dissolved metal concentrations can be measured by using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Alanlytik Jena model PlasmaQuant MS). The unfiltered samples were also later filtered using 0.20µm polysthersulfone filters (Macherey-Nagel GmbH & Co.KG) before using it for the ICP-MS analysis. 1ml of each of the samples were taken and diluted 10 times with 9.9ml ultrapure water, so that it falls within the range of the machine (in ppb).

The alternative method to determine the Fe total and dissolved Fe(II) concentrations used was the Fe colorimetric method. In this method a calibration line is obtained between the absorbance values in (A) and the Fe concentration values in mg/L. The slope of this line helps in determining the values of Fe(II) & total Fe concentrations. For Fe(II) measurements, 1-2ml of sample is added to 1ml of Fe trap to a 10mm plastic cuvette, which is finally filled upto 3.6ml with ultrapure water. The Fe(II) concentration values can be calculated by the reading of absorbance measured at 510 nm after 20 mins in the Genesys 10S UV-VIS User GUIDE Thermo Scientific Spectrophotometer. Similarly for total Fe measurements, about 1ml of hydroxyl-ammonium-chloride reducing agent is added with the sample into the Fe trap followed by adding ultrapure water upto 3.6ml in the cuvette. After a minimum of 1hr, the reading of absorbance at 510nm in the spectrophotometer will help in calculating the values of the Fe total concentrations.

The concentrations of the dissolved Mn was also detected by using HACH manganese kits (LCW632: 0.005-0.700 mg Mn/L). Separate 5ml samples were collected in 15 ml sample vials, at the start and the end of each experiment, which had to be filtered with 0.20µm polysthersulfone filters (Macherey-Nagel GmbH & Co.KG) first and then diluted with ultrapure water, to obtain the dissolved Mn concentration values. To these filtered samples, 0.5ml of reagent A is added followed by adding 0.5ml of reagent B, after which the sample tube is shaken vigorously and kept in a stagnant position for 5 mins. Finally, 1ml of reagent C is added to this mixture and again shaken vigorously. After a min, 5ml of these samples can be transferred to a 20mm plastic cuvette and then a reading of the dissolved Mn concentration can be taken in the DR 3900 Benchtop HACH Lange Spectrophotometer. Also, the pH & DO of the water samples during the experiments were monitored using a multimeter (WTW^{TM} Multi 3630 IDS).

After performing all the experiments, the filter media of MnO_2 was dried at 30°C in an oven for 24 hours after each experiment, to obtain a dry weight of about 4.960g of MnO_2 grains. Then the media was taken for analysis under the Digital Microscope VHX-5000 Series. Observations were compared for both before and after the experiments and various images of the media was taken at automated focus modes in order to see possibilities of Fe floc formation over these filter media as shown in (Figure 2.4).

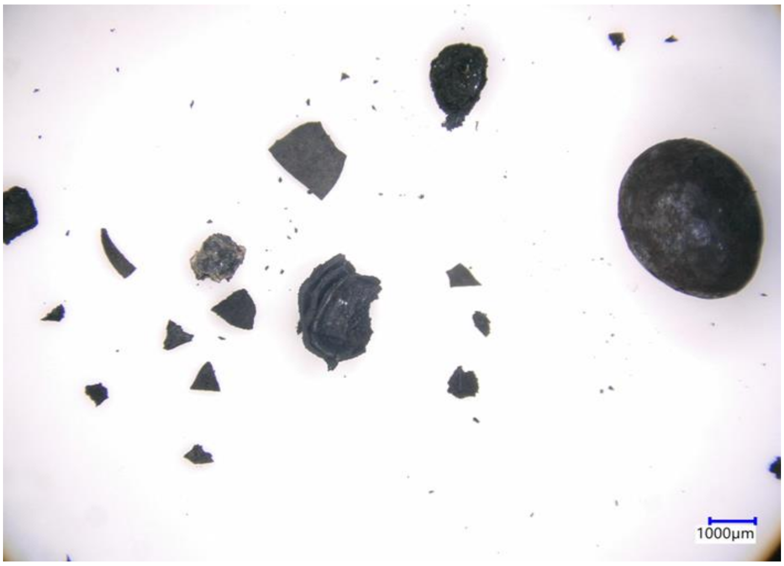


Figure 2.4: Microscopic view of a crushed MnO_2 grain (extracted from below 50cm of the Second NAF filter) from DWTP Vitens, Holten

2.4) Mass balancing of Mn & Fe interactions

Mass balancing can be a helpful tool to investigate the amounts of Fe oxidized to the amounts of Mn reduced with reference to equation(7). Also, from equations (8) and (9) described below, the mass balances of the different oxidation states of Mn(IV), Mn(III) and Mn(II) can be calculated:

$$\mathrm{Fe(II)(aq) + Mn(IV)(s) \rightarrow Mn(III)(s) + Fe(III)(s)} \qquad (8)$$

$$\mathrm{Fe(II)(aq) + Mn(III)(s) \rightarrow Mn(II)(aq) + Fe(III)(s)} \qquad (9)$$

By studying the differences in the measured and theoretical values, an estimation of how much iron or manganese is left unreacted or how much of each is either adsorbed or oxidized, and can be achieved via these balances. Identifying the molar ratios of how much iron is oxidized to how much manganese is reduced can be indicative of what form of redox processes are occurring in the filter and to understand the kinetics at varying filter conditions.

Stoichiometrically; from equation (7) we can say that 2moles of Fe(II) reacts with 1mole of Mn(IV) to produce 2moles of Fe(III) and 1mole of Mn(II). So, if the experimental concentration of dissolved iron, Fe(II) is $X=\frac{x(mg/L)*10^3}{(molar\ mass\ of\ Fe=55.845g/mol}$[µmol/L], and the initial Fe(II) stock dosed is of concentration y[µmol/L], then the corresponding theoretical amount of Fe(II) oxidized to Fe(III) is (y-X), which is the reacted Fe(II) concentration.

Similarly for Mn(II), if the experimental concentration of dissolved iron, Mn(II) is $X'=\frac{x'(mg/L)*10^3}{(molar\ mass\ of\ Fe=54.938g/mol}$[µmol/L], and the initial Mn(II) concentration, which in this case is 0[µmol/L], then the corresponding theoretical amount of Mn(IV) reduced to Mn(II) is (X'-0), which is the reacted Mn(II) concentration.

Therefore, if we have to calculate the molar ratios of Fe(II) oxidized: Mn(IV) reduced, we can simply divide $\frac{X}{X'}$. In this way, the comparison of the differences in the theoretical and experimental values of both Mn(II) and Fe(II) are studied in order to better understand the kinetic behaviour of each of them.

Also as mentioned before, there is a possibility that not all the Mn(IV) will be reduced to Mn(II) directly, but there might be an intermediate step of metastable Mn(III) solids production, which is defined by equations(8) and (9). The stoichiometry of the above reactions is assumed and the exact theoretical concentrations of Mn(III) and Mn(II) are not known but can be estimated. The theoretical Mn(II) value will be ½ of the total reacted Fe(II) value which is equivalent to the amount of reacted Mn(III) in equation(9). Also from equation(8), the amount of Mn(III) and Mn(IV) will be the difference of the total reacted Fe(II) value and the experimental Mn(II) value. The differences of the theoretical and the experimental values indicate the amount of unreacted Mn(III) and measured Mn(II) values.

3) Results

In this section the comparison of manganese removal rate in a full scale filter with the batch experiments involving MnO_2+Mn(II) system is done. Also, as mentioned in the hypothesis, the reduction of MnO_2 by Mn(II) and Fe(II) is discussed in this section by comparing it under pH = 6.5, 7.5 and 8.5. The variation in the reduction of MnO_2 and Mn(II) removal rate is studied under different anoxic as well as aerobic conditions and the kinetics for these reactions also have been investigated. Finally, the mass balancing of the Fe-Mn interactions were done to distinguish between differences in experimental and measured values.

3.1) Full scale Mn removal in the filter of WTP Holten

The preliminary observations seen in these Mn-Fe batch experiments was the change in colour of the solution. The colour of the water changed from colourless to orangish/brownish (typical of Fe(III) (oxyhydr) oxides) in experiments where dissolved Fe(II) was dosed to the water solution containing MnO_2 [Appendix 33 (C), 34 (C)]. It was also observed that the colour of the water changed from colourless to greyish/blackish in the experiments involving MnO_2 only or the experiments with dissolved Mn(II) [Appendix 33 (B), 34 (B)]. While the control experiment, involving only 10mg/L of Fe(II), turned orangish/brownish under aerobic conditions [Appendix 33 (D)], and remained colourless under anoxic conditions [Appendix 34 (D)]. These changes in colour can be a preliminary indication of manganese reduction or iron oxidation occurring in the system.

The filter media of the top 30cm filter depth appeared to be shiny grey as mentioned before, with minute sandy deposits on it which can be small deposits of Fe flocs or manganese oxides. The texture was hard and it was difficult to break it into pieces. However, when few of them were crushed, it appeared that there was a dark grey core inside, which was again covered by an outer layer of MnO_2 (Figure 2.3).

The total Mn, Fe and the NH_4 concentrations of the samples collected from Vitens, Holten were investigated by ICP-MS analysis and has been shown in (Figure 3.1 (A), (B)). Ideally all of the Mn, Fe and the NH_4 got removed by the time it reached the bottom of the filter.

According to the groundwater matrix of table 2.1, a total initial Mn concentration of 0.977mg/L, Fe concentration of 7.59mg/L and NH_4 concentration of 0.15mg/L was found entering the first filter unit. Here, a total of about 0.8 mg/L of Mn, 0.002 mg/L of Fe and 0.1 mg/L of NH_4 got removed. Only 18% of total Mn was removed in the first filter, whereas, almost 99.67% of total Fe was already removed in the first filter. The concentrations of total Mn (Figure 3.1 (A)), Fe and NH_4 (Figure 3.1 (B)), with respect to the height of the filter decreases to almost 0, when it reaches to a filter height of 1.5m. Hence, it can be said that ideally all of the Mn, Fe and the NH_4 gets removed by the time it reaches the bottom of the second filter.

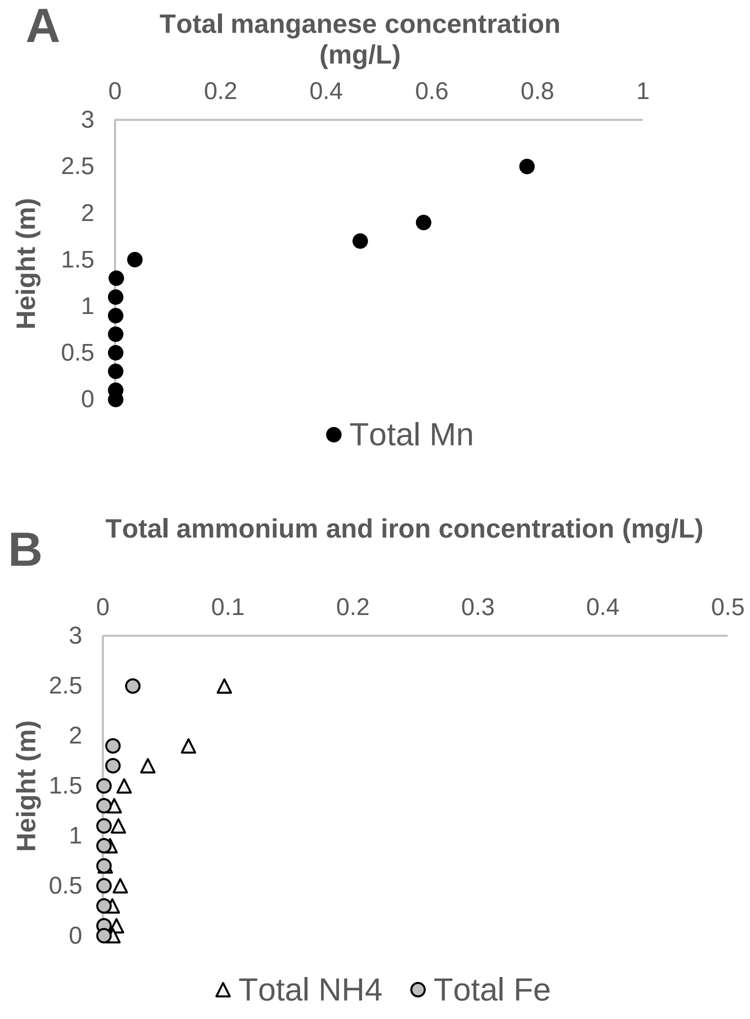


Figure 3.1: A) The measured total manganese concentration and B) the measured total ammonium & total iron concentration in mg/L with respect to the height of the second filter (Vitens, Holten) in metre.

3.2) MnO_2 reduction by Mn(II)

As mentioned in the method section 2.2, experiments with a system of MnO_2+Mn(II) were performed to further investigate the reduction of MnO_2 by the dosed 1mg/L Mn(II) in either an aerobic or an anoxic setup, or at different pH values (pH=6.5, 7.5, 8.5). However, there are some assumptions taken into account for these experiments, which are:

i) All MnO_2 is considered to be of the Mn(IV) form at the start of the experiments.
ii) All the dissolved manganese is assumed to be of Mn(II) form.
iii) Theoretically, the reacted Mn(IV) which remains unaccounted for products formed such as dissolved manganese, is assumed to be Mn(III), that was never reduced to Mn(II) or re-reacted Mn(II) to form fresh Mn(III).

Experiments which involve such a system under both aerobic and anoxic conditions performed at different pH values (pH=6.5, 7.5, 8.5) has been shown (Figure 3.2 (A), (B)). These experiments were done to study the effect of DO and pH in the oxidation of the dissolved manganese in an MnO_2+Mn(II) system. . It was observed that in an aerobic system, at pH=7.5, about 0.103 mg/L of dissolved manganese remained after 10 mins of experimentation, whereas for the same pH in an anoxic system, about 0.148mg/L of dissolved manganese was left. Hence, almost 0.045mg/L additional Mn(II) was available in an anoxic system, which means that the oxidation in the presence of DO is higher. Also, for both the systems, it was seen that there has been an optimal manganese oxidation at pH=7.5. Hence, in an overall nutshell, these results mean that even in the absence of any external oxygen, there is oxidation of the dissolved manganese by these manganese oxides, and it is not only optimum at a higher pH of about 7.5 but also faster under higher DO, which complies with the discussion put forward in the introduction section. This clearly indicates that MnO_2 with the presence of O_2 enhances the manganese oxidation rate and both the MnO_2 and O_2 can act as oxidizing agents to contribute to a faster oxidation.

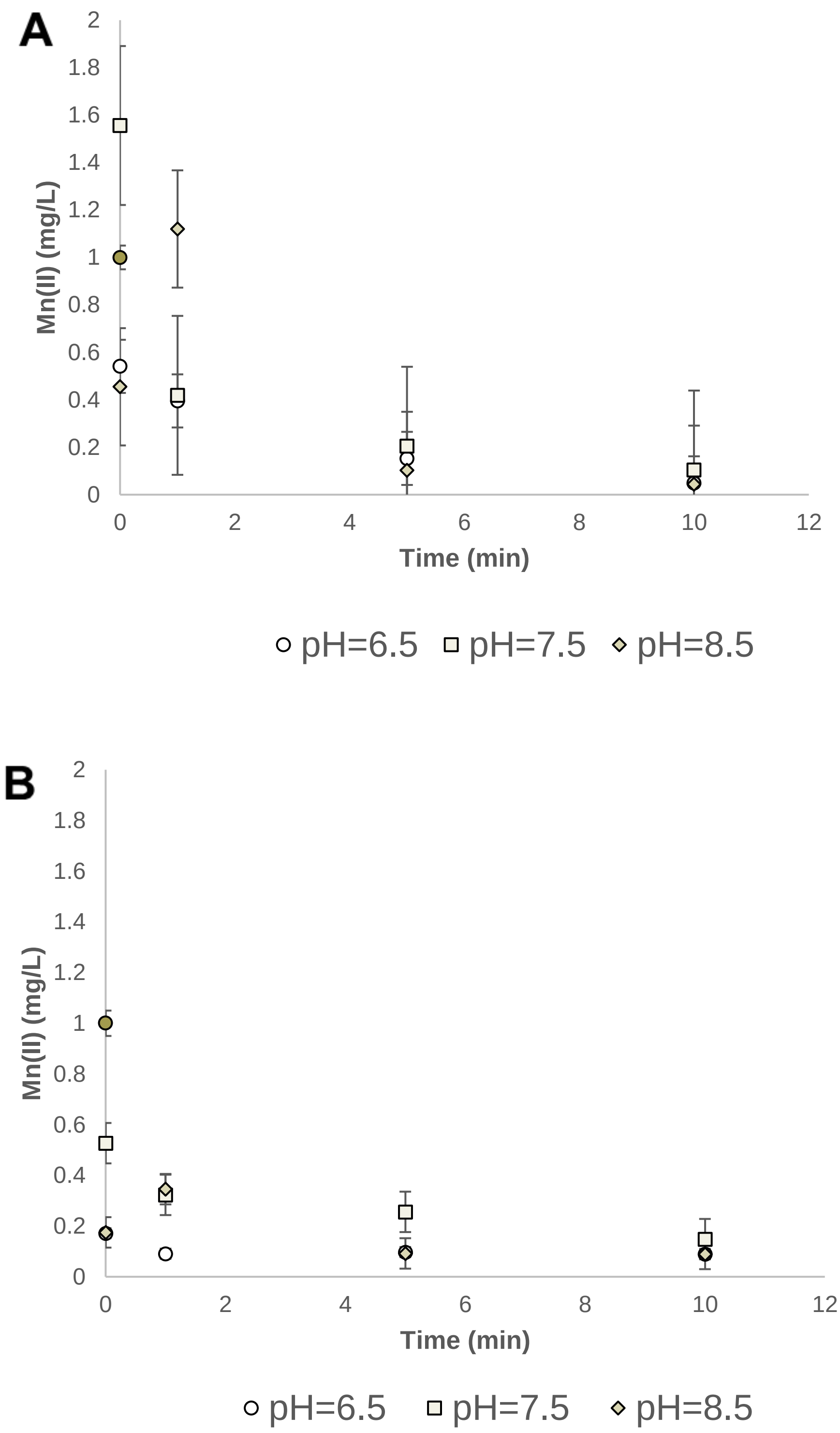


Figure 3.2: Concentration of the measured dissolved manganese oxidized at different pH = 6.5, 7.5 and 8.5 in the experiments with MnO_2+Mn(II) system involving 20g/L MnO_2 (Holten filter media) and 1mg/L dosed Mn(II) for 10 minutes in (A) aerobic condition [DO=8-9 mg/L] and (B) anaerobic condition [DO=0.0-0.03 mg/L]

In order to investigate how this rate of manganese oxidation varies in both the aerobic and anoxic conditions, a study of the kinetics is done (Figure. 3.4 (A), (B)). The rate and the order of the reactions are found to quantitively depict the manganese oxidation rates.

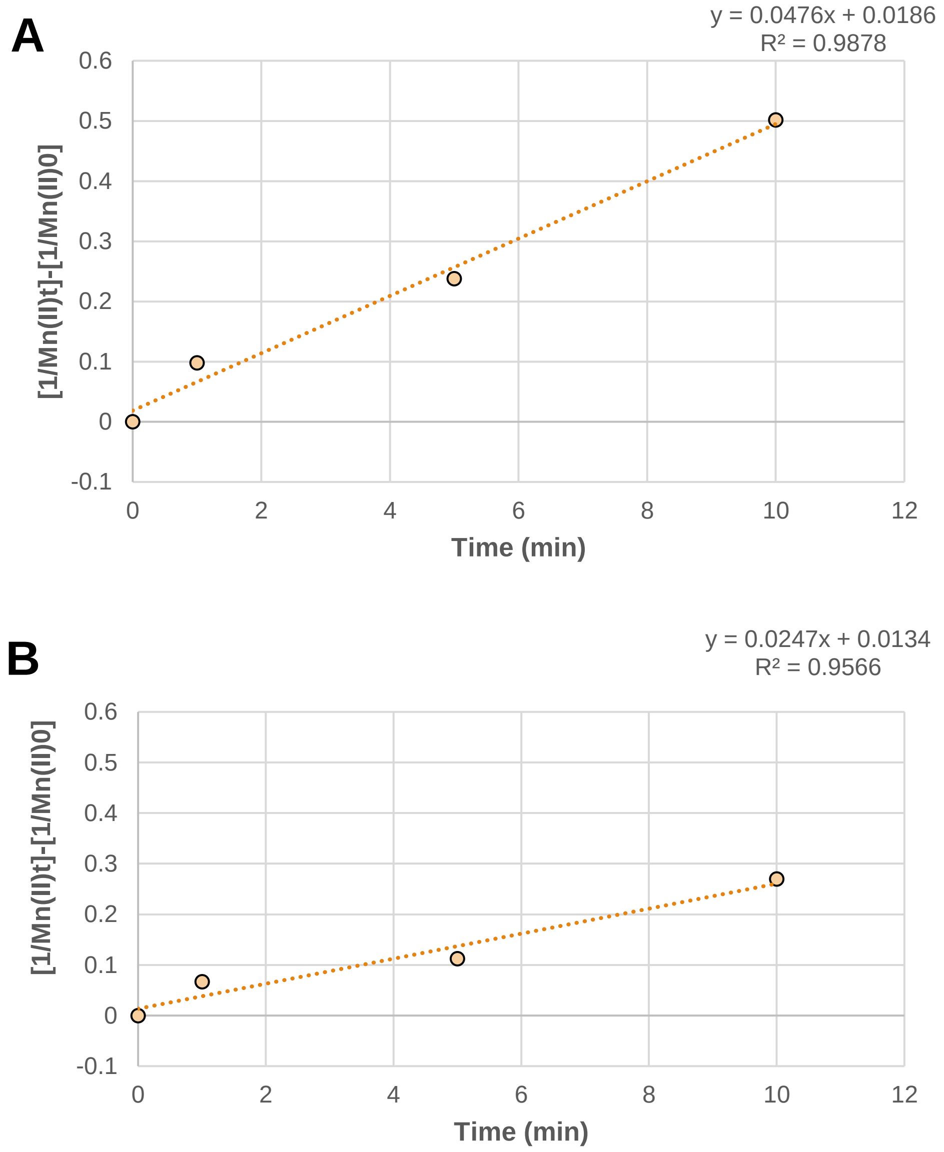


Figure 3.4: A) Kinetics for Mn(II) oxidation under aerobic [DO = 0.0-0.03 mg/L] and (B) anoxic [DO = 8-9mg/L] conditions in MnO_2+Mn(II) system involving 20g/L MnO_2 (Holten filter media) and 1 mg/L dosed Mn(II) [pH=7.5]

It was found that both conditions followed a reaction rate of order 2. However, the rate constant of the aerobic system was about 0.0476 $\mu mol^{-1} min^{-1}$, while for the anoxic system it was about 0.0247 $\mu mol^{-1} min^{-1}$. It can be clearly observed that the reaction rate of the aerobic system is almost 2 times faster than the anoxic system, which also depicts the faster manganese removal rate in an aerobic system. Here, phenomenon like adsorption is not taken into consideration but will be an interesting point to discuss in the following chapters.

3.3) MnO_2 reduction by Fe(II)

After studying the reduction of MnO_2 by Mn(II), or alternatively, the oxidation of Mn(II) by MnO_2, systems of MnO_2+Fe(II) were studied, by dosing about 10mg/L of Fe(II) to the system. This was done to study the possible reduction of MnO_2 by the dosed Fe(II). Experiments were performed in either an aerobic or an anoxic setup, or at different pH values (pH=6.5,7.5,8.5). The assumptions considered were similar to that mentioned in section 3.2.

The effect of pH in the removal efficiencies of dissolved manganese under anoxic conditions (DO=0.0-0.03mg/L) and at different pH values (pH=6.5,7.5,8.5) has been shown (Figure 3.5). It was observed that at pH=7.5, about 1.52 mg/L of Mn(IV) was reduced. However, about 1.29mg/L at pH=6.5 and about 0.66mg/L at pH=8.5 of reduced Mn(IV) was measured. Hence, it is clear that in the absence of any external oxygen in the system, there is a reduction of Mn(IV), or a possible mobilization of the dissolved manganese, which is again optimum at pH=7.5.

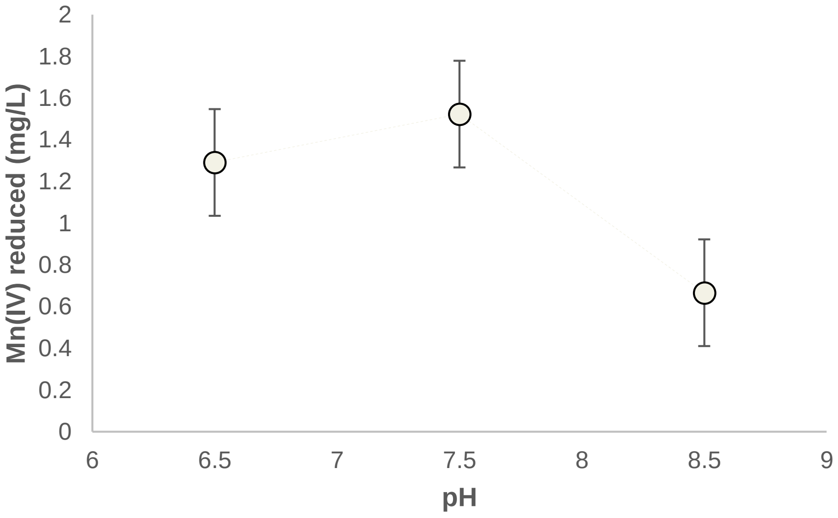


Figure 3.5: Concentration of the measured Mn(IV) reduced at different pH = 6.5, 7.5 and 8.5 in the experiments with MnO_2+Fe(II) system involving 20g/L MnO_2 (Holten filter media) and 10mg/L dosed Fe(II) for 10 minutes [DO=0.0-0.03 mg/L]

Here, interesting will be to exactly find whether there is a release of Mn(II) in such MnO_2+Fe(II) systems, where there is no external Mn(II) dosage. Hence, to find out the possibilities of Mn(II) mobilization and compare the manganese reduction efficiencies under an aerobic and an anoxic MnO_2+Fe(II) system, the following comparative analysis was done as shown (Figure 3.6). It was also observed that there was Mn(II) released in both the aerobic and anoxic conditions, which was mainly hypothesized before.

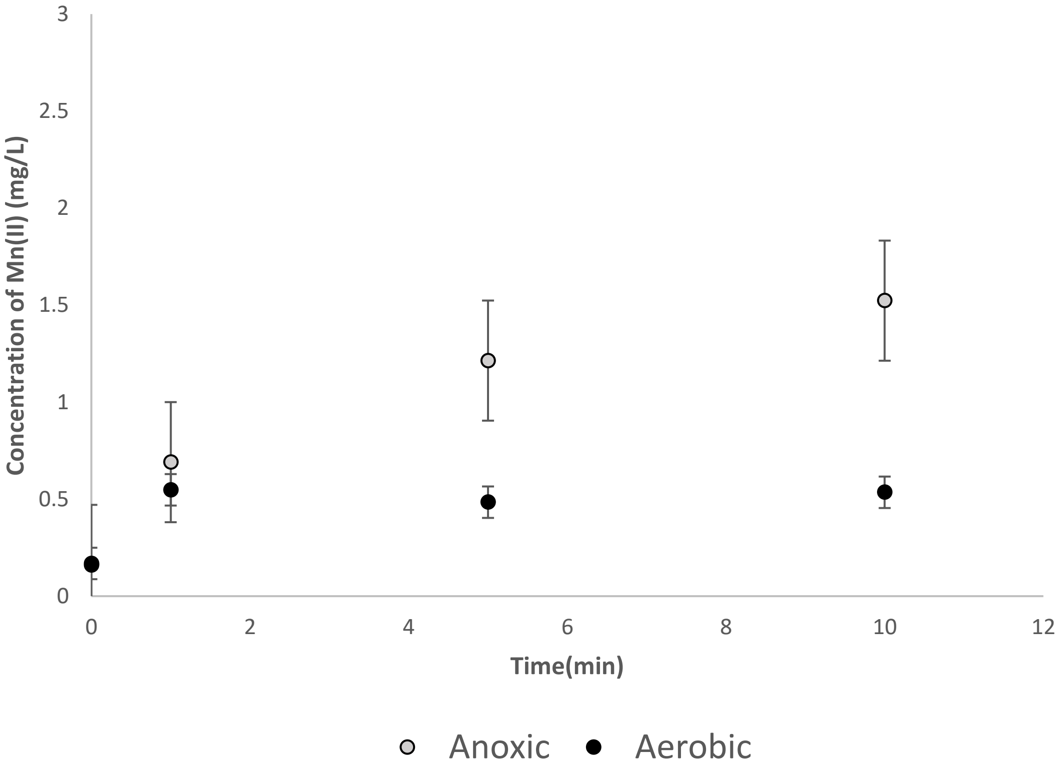


Figure 3.6: Concentration of the measured dissolved manganese oxidized under anoxic [DO = 8-9mg/L] and aerobic [DO = 0.0-0.03 mg/L] conditions in the experiments with MnO_2+Fe(II) system involving 20g/L MnO_2 (Holten filter media)and 10mg/L dosed Fe(II) with respect to run time in minutes [pH=7.5]

About 2.36mg/L of dissolved manganese was mobilized in the anoxic system, whereas only 0.38mg/L was oxidized in the aerobic system. This indicates that almost 6.21 times higher Mn(II) is mobilized in an anoxic system than compared to that in aerobic. Also, after the first minute, there was no additional Mn(II) released in such systems under the aerobic conditions and remained at 0.38mg/L for 10 minutes. This can be indicative of the hinderance in the reduction capacity of Mn(IV) to completely get reduced to Mn(II) under the presence of both O_2 and MnO_2. Upon studying the kinetics, it was found that for manganese reduction under anoxic conditions, the reaction rate was of order 0 and the rate constant was about 1.1641 μmol min^{-1} (Appendix 43). However, under aerobic conditions, the reaction rate was of order 2 and the rate constant was about 0.0024 μmol^{-1} min^{-1} (Appendix 44).

Simultaneously, it was observed that there was also oxidation of the dosed Fe(II) in such a system. Experiments of MnO_2+Fe(II) systems were performed at pH=6.5, 7.5 and 8.5, under anoxic conditions, to investigate the influence of pH in the Fe(II) oxidation (Figure 3.7). At the very first minute of the experiments, the Fe(II) concentration was already lowest at pH=8.5, being 1.13mg/L, followed by 3.9mg/L at pH=7.5 and highest at pH=6.5 with 5.29mg/L. Almost all the Fe(II) disappeared beyond 2 mins at pH=8.5. At time t=5 mins, Fe(II) concentration was lowest at pH=8.5 with 0.1mg/L, followed by 1.8mg/L at pH=7.5 and highest being at pH=6.5 of 3.1mg/L. Hence, it can be observed that as the pH of the solution increases, the Fe(II) oxidation rate becomes faster.

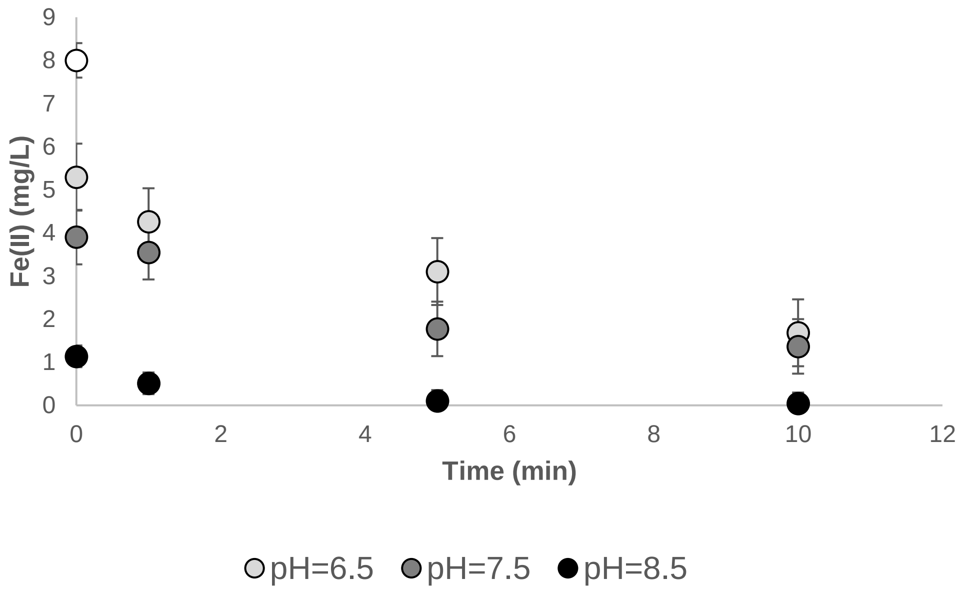


Figure 3.7: The concentration of measured Fe(II) with experiments involving 20g/L MnO_2 (Holten filter media) and 10mg/L dosed Fe(II) at pH=6.5, 7.5 and 8.5 [DO=0.0-0.03 mg/L]

To further compare this rate of iron oxidation in both the aerobic and anoxic conditions, a study of the kinetics is done (Figure 3.8). The rate and the order of the reactions are found to quantitively depict the iron oxidation rates.

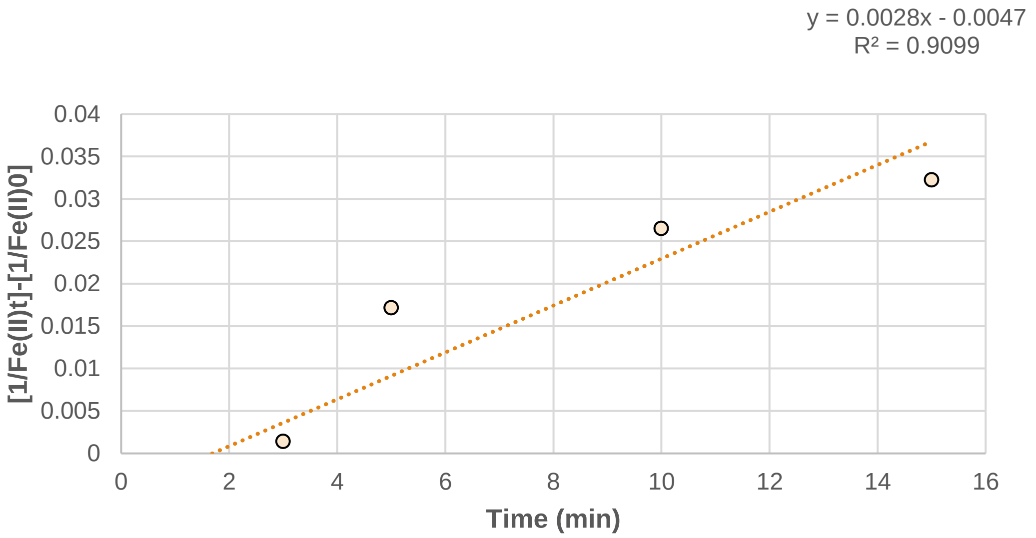


Figure 3.8: Kinetics for Fe(II) oxidation under anoxic [DO = 8-9mg/L] conditions in MnO_2+Fe(II) system involving 20g/L MnO_2 (Holten filter media) and 10 mg/L dosed Fe(II) [pH=7.5]

Iron can typically follow both first and second order kinetics for pH greater than 7 with a half-life of about 12 minutes (Sung & Morgan, 1980). Similarly, in this research, it was found that iron oxidation under anoxic conditions followed a reaction rate of order 2. Also, the rate constant of the anoxic system was about 0.0028 $\mu mol^{-1}min^{-1}$ only. When compared with the aerobic system, it can be clearly observed that the reaction rate of the aerobic system is approximately 65.39 times faster than the anoxic system (Appendix 42), which is quite high. Additionally, it was found that the iron oxidation rate was much faster than the rate of manganese oxidation, under the specified experimental conditions, occurring in natural groundwaters (Katsoyiannis & Zouboulis, 2004). The faster rates of Fe(II) oxidation were also due to catalysis by FeOOH, which can enhance the rate by a factor up to 10 (Katsoyiannis & Zouboulis, 2004).

3.4) Mass balancing of Mn & Fe interactions

For a better understanding of these manganese and iron interactions in an MnO_2-Fe(II) system, the molar ratios of the iron oxidized to manganese reduced is calculated in such a system, under anoxic conditions (in the absence of any other external oxidizing agent like O_2). The concentrations of both Mn(II) and Fe(II) were plotted with respect to experimental run time as shown in (Figure 3.9) and (Figure 3.10) respectively. It was observed that there was a continuous increase in Mn(II) concentration from 2.9µmol/L to 43.1 µmol/L corresponding to a net increase of 40.2 µmol/L, which is a significant increase in 30 mins. There was a steep increase of about 19.2 µmol/L of Mn(II) concentration from t=2mins to t=5mins.

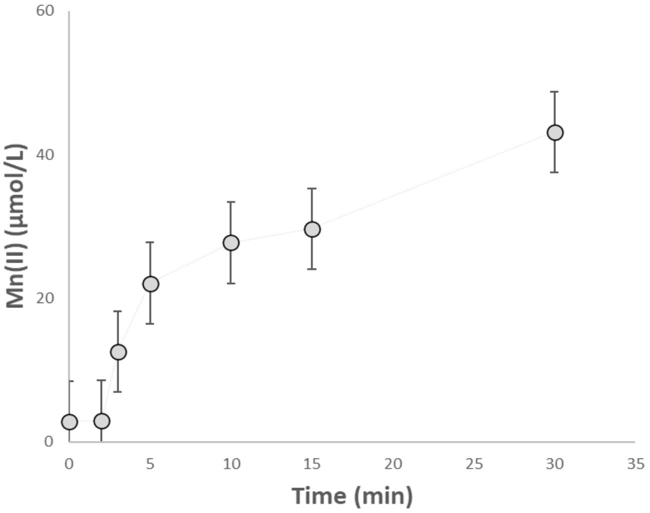


Figure 3.9: The concentration of the measured Mn(II) with experiments involving 20g/L MnO_2 (Holten filter media) and 10mg/L dosed Fe(II)
[pH=7.5,DO=0.0-0.03 mg/L]

Out of the dosed 179.06 µmol/L Fe(II) (equivalent of 10mg/L of dosed Fe(II)), almost 148 µmol/L of Fe(II) got quickly oxidized in the first 5 mins, after which it almost remained the same upto t=30mins. Although, not all the Fe(II) got oxidized by the end of the experiment, with a remaining amount of 21.2 µmol/L Fe(II) present in the solution. Hence, this can also indicate a possibility of hinderance of the Mn(II) released by the MnO_2 filter media in the Fe(II) oxidation processes or that a part of the Fe(II) not only got oxidized to Fe(III)oxides but also got adsorbed on the MnO_2 filter media and was not obtained in the solution.

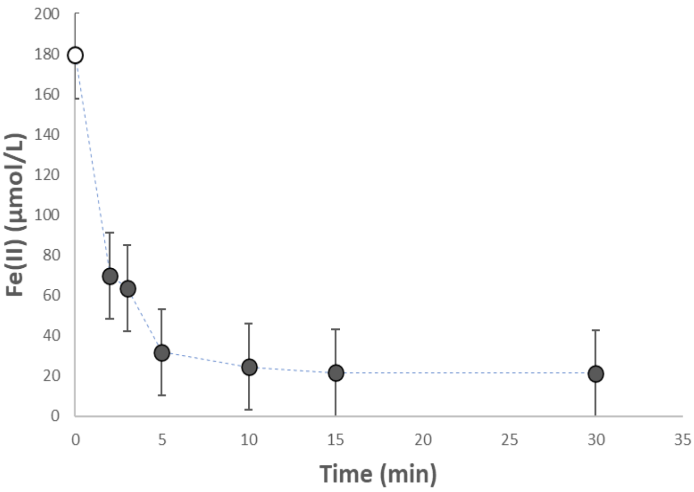


Figure 3.10: The concentration of the measured Fe(II) with experiments involving 20g/L MnO_2 (Holten filter media) and 10mg/L dosed Fe(II) [pH=7.5,DO=0.0-0.03 mg/L]

Mass balancing in such a system of MnO_2-Fe(II) has been done and the theoretical vs measured values of dissolved Mn has been graphically interpreted below, in the (Figure 3.11 (A)). The reaction taking place in the system is:

$$2Fe(II)+MnO_2+4H^+ \rightarrow Mn(II)+2Fe(III)+2H_2O$$

Theoretically;

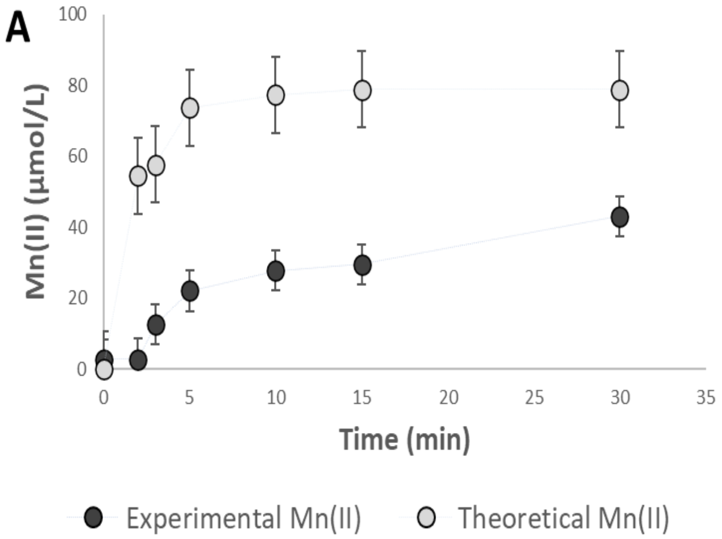
2moles of Fe(II) produces 1mole of Mn(II);

OR/ 2moles of Fe(II) when gets fully oxidized to 2 moles of Fe(III), then per 2moles of Fe(III), 1mole of Mn(II) is formed. Therefore, when calculating the theoretical values of Mn(II) and Fe(II) at the beginning and the end of the experiments indicates that:

When 10mg/L of initial Fe(II) is dosed in the system, it shall give a theoretical value of 179.06µmoles/L of Fe(II) at the start of the experiment (Figure 3.10). Parallely, if all the Fe(II) is considered to react with MnO_2, then it shall produce 179.06/2 µmoles/L of Mn(II) at the end of the experiment. It can be seen that almost (179-69)=110 µmoles/L of Fe(II) rapidly got oxidized in the early 2 mins of the run time, reducing to about 21 µmoles/L of Fe(II) at the end of run time.

Similarly, the effect on the concentration of Mn(II) throughout the same experiment follows a similar pattern. It was found that the reduction and release of manganese ions did occur and this manganese ion released is positively correlated with the concentration of ferrous ion (Huiping et.al,2020). Interesting point here is the difference between the theoretical dissolved Mn value and the measured dissolved Mn value at the end of the experimental runtime. It seems that about (89.53-43.12)=46.14 µmoles/L Mn(II) remains unreacted at t=30mins. There is clearly a manganese gap which can imply that a part of the Mn(II) is either re-oxidizing to solid Mn(III) or is fully oxidized to Mn(IV) as mentioned in the assumptions. Hence, the full reduction to 89.53 µmoles/L of Mn(II) hasn't taken place. Also, it can be said that Mn(II) is a reduction product of Mn(IV) & Fe(II), although the stoichiometric ratio was not achieved. Mn(IV) acts as an electron acceptor in such conditions when there is absence of O_2.

In (Figure 3.11(A)), there is also a lag observed between the experimental Mn(II) and theoretical Mn(II) values, throughout the experiments. There is about 40µmol/L of unreacted/unaccounted Mn(II) released in the end of the runtime.



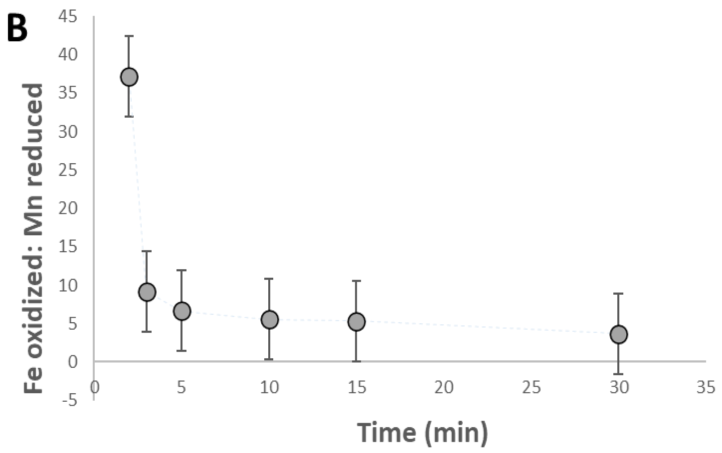


Figure 3.11:A) The concentration of experimental measured dissolved Mn(II) & theoretical calculated dissolved Mn(II), B) the ratio of Fe oxidized: Mn reduced with experiments involving 20g/L MnO_2 (Holten filter media) and 10mg/L dosed Fe(II) with respect to run time in minutes [pH=7.5,DO=0.0-0.03mg/L]

Finally, mass balances at each of the time intervals have been performed and the molar ratios of dissolved Fe(II) or the Fe(II) reacted: dissolved Mn(II) reduced have been calculated and plotted (Figure 3.11(B)). Mathematically; the molar ratios of dissolved Fe oxidized: dissolved Mn reduced in such systems are shown below in table 3.1. The dissolved manganese was found to be reduced in such sytems, reaching Fe(II) : Mn(II) ratio of 3.65 at the end of 30 mins.

Table 3.1 Molar ratios of dissolved Fe oxidized : dissolved Mn reduced in Fe(II)-MnO_2-N_2 system

Time interval(mins)	Fe oxidized: Mn reduced
0-2	37.22
2-3	9.18
3-5	6.66
5-10	5.57
10-15	5.31
15-30	3.65

Also it is seen that there is a sharp decrease in the Fe : Mn ratio from 37.22 to 9.18 from time intervals 0-2 mins to 2-3mins. This implies the faster oxidation rate of Fe(II) to Fe(III) than any possible initial Mn(II) reduction in the system. But from time interval 3-5 mins onwards, the molar ratios of Fe:Mn decreases very gradually becoming 6.66, further reducing to 3.65 at time interval 15-30mins. This can imply that since most of the Fe(II) has already oxidized, there is a gradual shift of more Mn(II) reduction happening towards the end of the experiment than at the beginning.

4) Discussion

This section compares the manganese removal rate under anoxic vs aerobic environments and that of the possibilities of adsorption or oxidation mechanisms. All the manganese re-mobilization and re-oxidation pathways are also discussed here.

4.1) Anoxic vs Aerobic Mn removal

As discussed in results, it was observed that under the aerobic conditions, the Mn(II) removal efficiency is more than that in anoxic conditions (Figure 4.1). The manganese removal efficiencies are about 43.79% higher at pH=6.5, 21.28% at pH=7.5 and 41.75% at pH=7.5, in an aerobic system than compared to the aerobic one. However, the optimum manganese removal is at about 93.31% at pH=7.5 under aerobic conditions and the lowest at about 47.59% at pH=6.5 under anoxic condition.

From the studies done by (Buamah, 2009), it was observed that the manganese removal efficiency was dependent on the pH of the solution, which also influenced the solubility of Mn(II). At a particular HCO_3^- concentration, the solubilities of the dissolved manganese decreased in increasing pH as mentioned earlier. A raised pH increases manganese oxide concentration on the grain, and the presence of an oxidant, which in this case both MnO_2 & O_2, speeds up the adsorption (Piispanen & Sallanko, 2010). Also, an increased manganese oxide concentration enhances the manganese removal indirectly by increasing the number of adsorption sites (Piispanen & Sallanko, 2010). From the research findings of (Piispanen & Sallanko, 2010), it was found that the adsorption is 80% slower at pH 6 than at pH 8. At a pH higher than 8, Mn(II) is converted to relatively insoluble (hydr)oxides present as mixed oxidation state species (Chiswell & Huang, 2006), and one cannot also assume that insoluble manganese oxide species in low pH waters will dissolve rapidly. The solubility of such oxides is generally low, and thus dissolution is kinetically slow and hence, at a lower pH, the Mn(II) removal efficiency is less. In general, an increase in pH shows improved Mn removal and is effective at pH values between 7.1 and 8.0 (Bruins, 2016). Also, a higher pH strongly can enhance adsorption of Mn(II) (Buamah, 2009) and can support both heterogeneous as well as autocatalytic manganese adsorption or oxidation.

Also, the high adsorption ability of manganese dioxide for cationic species is well-documented (Stumm & Lee, 1961) and when O_2 is present as an additional electron acceptor, the manganese removal is very efficient. From (Stumm and Morgan, 1996), it is known that the manganese removal is negatively affected by the absence of, or low concentration of dissolved oxygen. Moreover, (Bruins, 2016) had done a detailed analysis of the manganese removal efficiencies of a few water treatment plants and it was seen that the manganese removal was poor when the dissolved oxygen was less than 1 mg/L. When there is a shortage of oxygen, a reducing environment is created and Mn(II) instead of oxidizing to Mn(III) or Mn(IV) oxidation states, starts leaching in the system. Hence, there has to be a minimum concentration of DO present in the solution support manganese removal by either manganese adsorption or oxidation (Bruins, 2016).

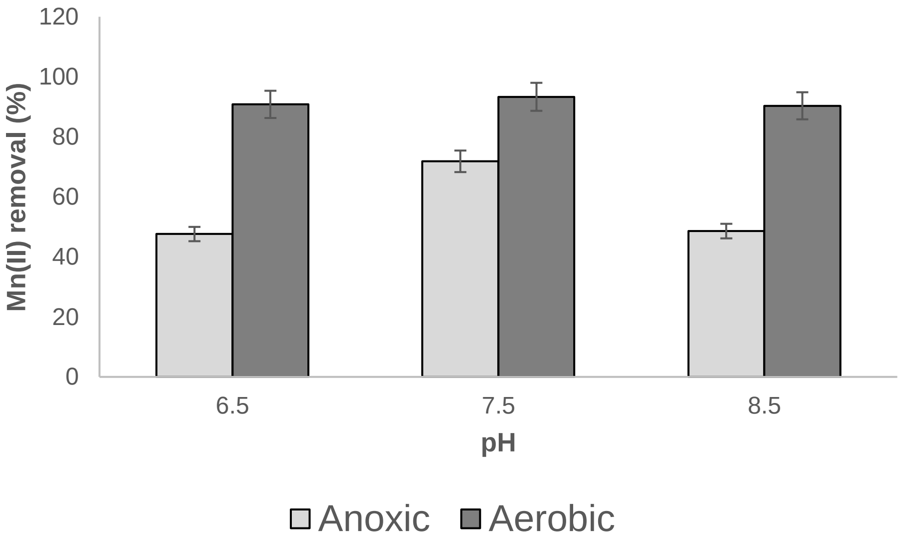


Figure 4.1: The removal percentage of the dissolved manganese with varying pH and aerobic/anoxic conditions with experiments involving 20g/L MnO_2 (Holten filter media) and 1mg/L dosed Mn(II).

4.2) Adsorption vs Oxidation

From assumption(iii) of section 3.2, it was stated that theoretically, the reacted Mn(IV) which remains unaccounted for products formed such as dissolved manganese, and is assumed to be Mn(III), that was never reduced to Mn(II) or re-reacted Mn(II) to form fresh Mn(III). Accordingly, the calculations of mass balancing from equations (8) and (9) of section 2.5, to estimate the Mn(II) aqueous and Mn(III) solid concentrations formed throughout the experiment containing an MnO_2-Fe(II) system, were done and plotted against time (Figure 4.2).

Although, the amount of Mn(II) increased as the mobilization started, but the amount of calculated solid Mn(III) decreased simultaneously by the end of 30 mins. In a previous study from (Cheng et al., 2019), one possible pathway for Mn removal was proposed for a low DO concentration. That is, Mn(II) in solution (Mn(II)(aq)) is firstly absorbed onto vacancy defect, and (Mn(II)) then transforms into Mn(II) in the layer ($Mn(II)_{layer}$) before $Mn(II)_{layer}$ is oxidized by Mn(IV) in the layer ($Mn(IV)_{layer}$) to form Mn(III) via a disproportionation reaction. Although there is no consumption of DO, the removal of Mn will consume Mn(IV), thereby resulting in the impossibility of continuous Mn removal, which is inconsistent with the continuous Mn removal performance under anaerobic conditions. It is also found that Mn(II) in solution is mostly converted to the solid phase Mn(II) of the Fe–Mn co-oxide under anaerobic conditions due to the high surface Mn(II) content and no DO consumption (Cheng et al., 2020). Also, from (Figure 4.3), it can be concluded that the difference of the theoretical and the experimental Mn(II) values gradually decreased throughout the experimental duration, which can indicate that there has been a portion of reduced Mn(III) which has been unaccounted for, or did not completely reduce to Mn(II).

In the paper of (Gude et al., 2017), experiments were performed by dosing 2mg/L of Mn(II) in an Fe(II)+MnO_2 system and it was found that in the presence of Fe(II), there was an increased Mn(II) concentration. The mobilisation of Mn(II) from the MnO_2, even in the presence of 2mg/L Mn(II), is a clear indication that Fe(II), independent of Mn(II) concentrations, was active on the MnO_2 surface and was the preferred ion by the MnO_2 mineral surface. For Mn(II) addition to the MnO_2, a similar explanation as for Fe(II) is justified since Mn(II) does not oxidise homogenously in aerated water at pH 7 (Diem and Stumm, 1984) and there was an observed loss in dissolved Mn(II) of about 30%. Therefore, the Mn(II) must have been retained on the MnO_2 surface, which could have led to similar surface passivation of the MnO_2 as Fe(II).

Therefore, there is a possibility that the adsorbed Fe(II) may inhibit the complete oxidation or reduction pathways of manganese. Another possibility is the deposition of Mn(III) over the MnO_2+Fe floc particles having an overall impact in slowing down the manganese release from these MnO_2 particles.

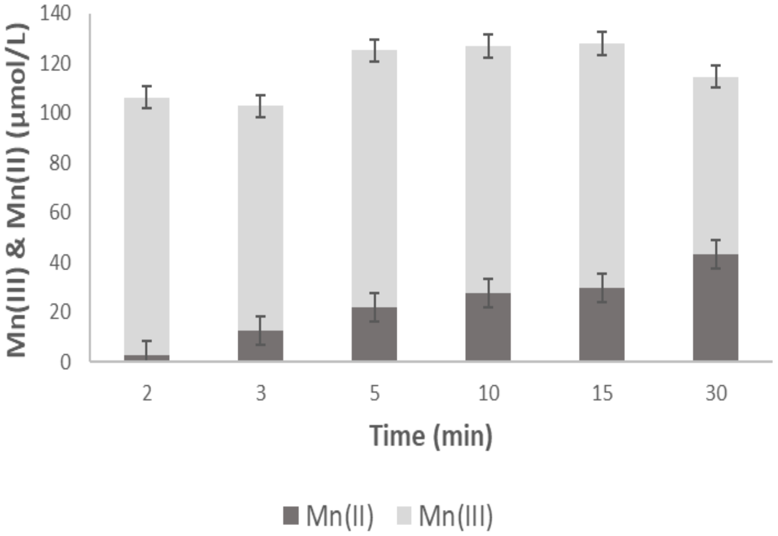


Figure 4.2: The concentrations of calculated Mn(II) & Mn(III) with respect to experimental runtime involving 20g/L MnO_2 (Holten filter media) and 10mg/L dosed Fe(II) [pH=7.5, DO=0.0-0.03mg/L]

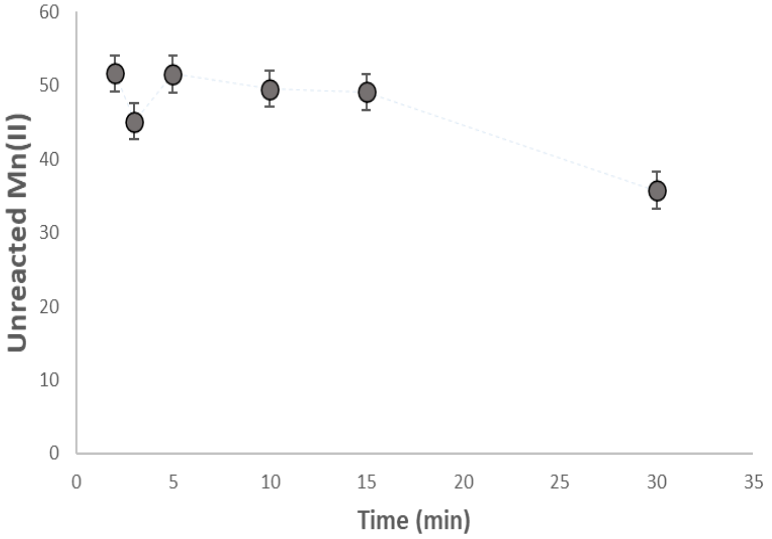


Figure 4.3: The calculated unaccounted Mn(II) concentrations with respect to experimental runtime involving 20g/L MnO_2 (Holten filter media) and 10mg/L dosed Fe(II) [pH=7.5, DO=0.0-0.03mg/L]

4.3) Mn reduction and oxidation pathways

From (Figure 1.5) of the introduction chapter, based on the descriptions of various conditions and parameters from the methods and results that effect the manganese reduction and oxidation pathways, a total of 6 major manganese redox pathways were found to be developed as shown in (Figure 4.4). By varying the levels of pH from 6.5 to 8.5, in the presence or absence of O_2, interactions when there is a dosage of Fe(II) to the system, the reduction and oxidation pathways has been studied. The primary finding of this research is the manganese mobilization. When there is a presence of Fe(II) or Mn(II), there is manganese mobilization or conversion of Mn(IV) to Mn(II) following path 5, simultaneously oxidizing Fe(II) to Fe(III)oxides. But this release in manganese doesn't always occur directly, and is depending on the availability of DO and variation in pH conditions. It can either form intermediate metastable Mn(III) solids on top of MnO_2 surfaces, as discussed in the previous sections, shown by path 1, under anoxic conditions and a pH ranging from 6.5-7.5, and then upon further exposure to a reducing environment with a lesser DO, ultimately forming Mn(II) solids following path 2 under pH=6.5.

Again when these Mn(II) solids under the presence of both O_2 and MnO_2, can get partially re-oxidized to Mn(III) solids at a pH of 7.5 shown by path 3. As mentioned above in the literature, that not only the O_2 but also the Mn(IV) present in the solution can help in the Mn(II) oxidation processes. Similarly, upon increasing the pH from 7.5-8.5, under the presence of O_2, the MnO_2 can enhance further oxidation of Mn(III) solids back to Mn(IV), shown by path 4. Ultimately, at a pH of 8.5, most of the Mn(II) oxidizes to Mn(IV) under ideal aerobic environment shown by path 6. For an added understanding, [Appendix 45] can be referred for a more descriptive Mn cycle depending on pH and DO sensitivities. All of these is because the solubility of manganese is low at lower pH, which might lead to the presence of more Mn(II)/Mn(III)/Mn(IV) forms (Chiswell & Huang, 2006) and as mentioned in section 4.1, both MnO_2 and O_2 together enhance the rate of manganese oxidation.

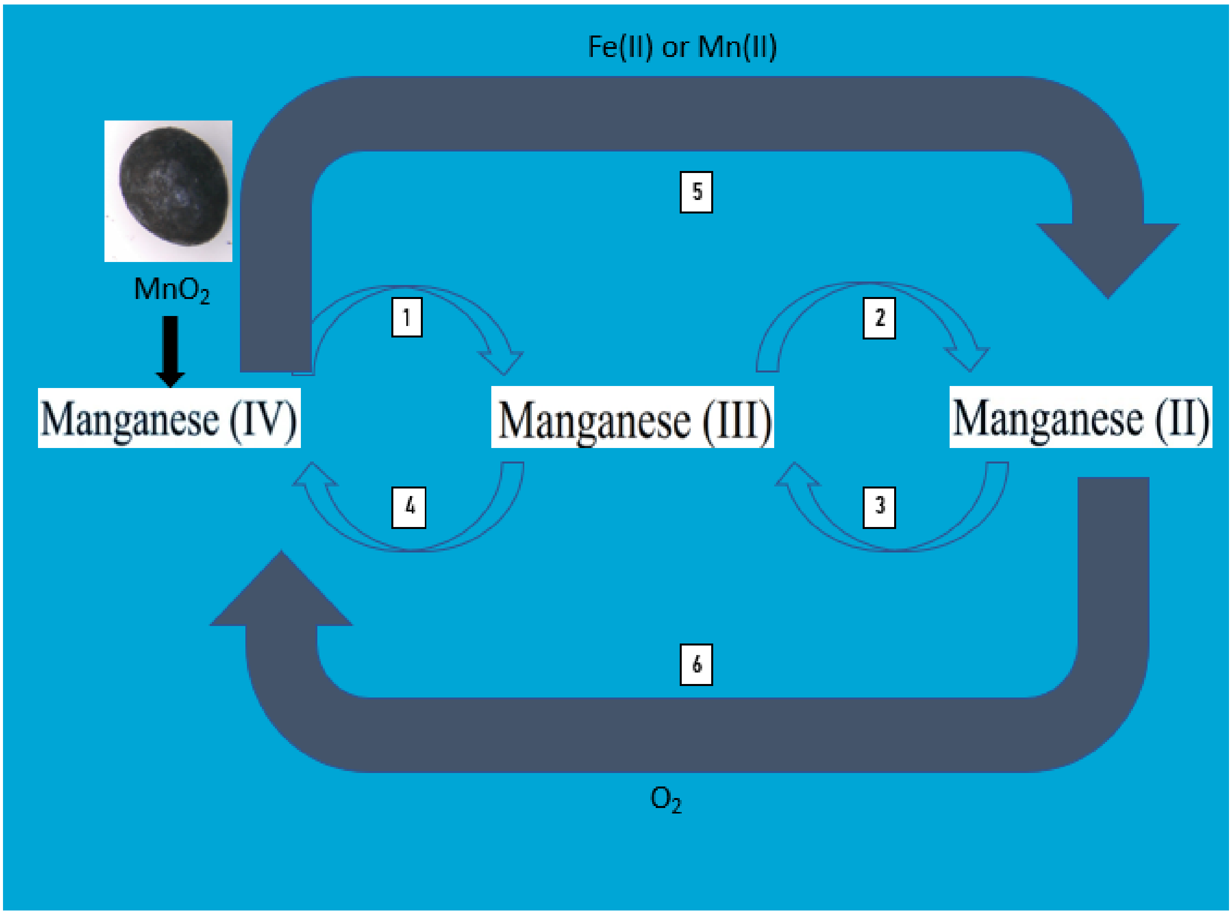


Figure 4.4: Manganese redox pathways based on different conditions

A representative sketch of all the other possible manganese redox interactions from one oxidation state to another is shown below (Figure 4.5 (A), (B)). From all the experimental analysis, it can be inferred that all these interactions are not only active under anoxic conditions, but also occurs under aerobic conditions. Interestingly, these different forms of Mn and Fe also interact between each other either as oxidants or reductants. Mn(IV) gets reduced to Mn(III) either via simultaneous oxidation of Mn(II) to Mn(III)/Mn(IV); or Fe(II) to Fe(III). The produced Mn(III) intermediates can also re-oxidize back to Mn(IV) by previously formed Mn(III) solids as reactants.

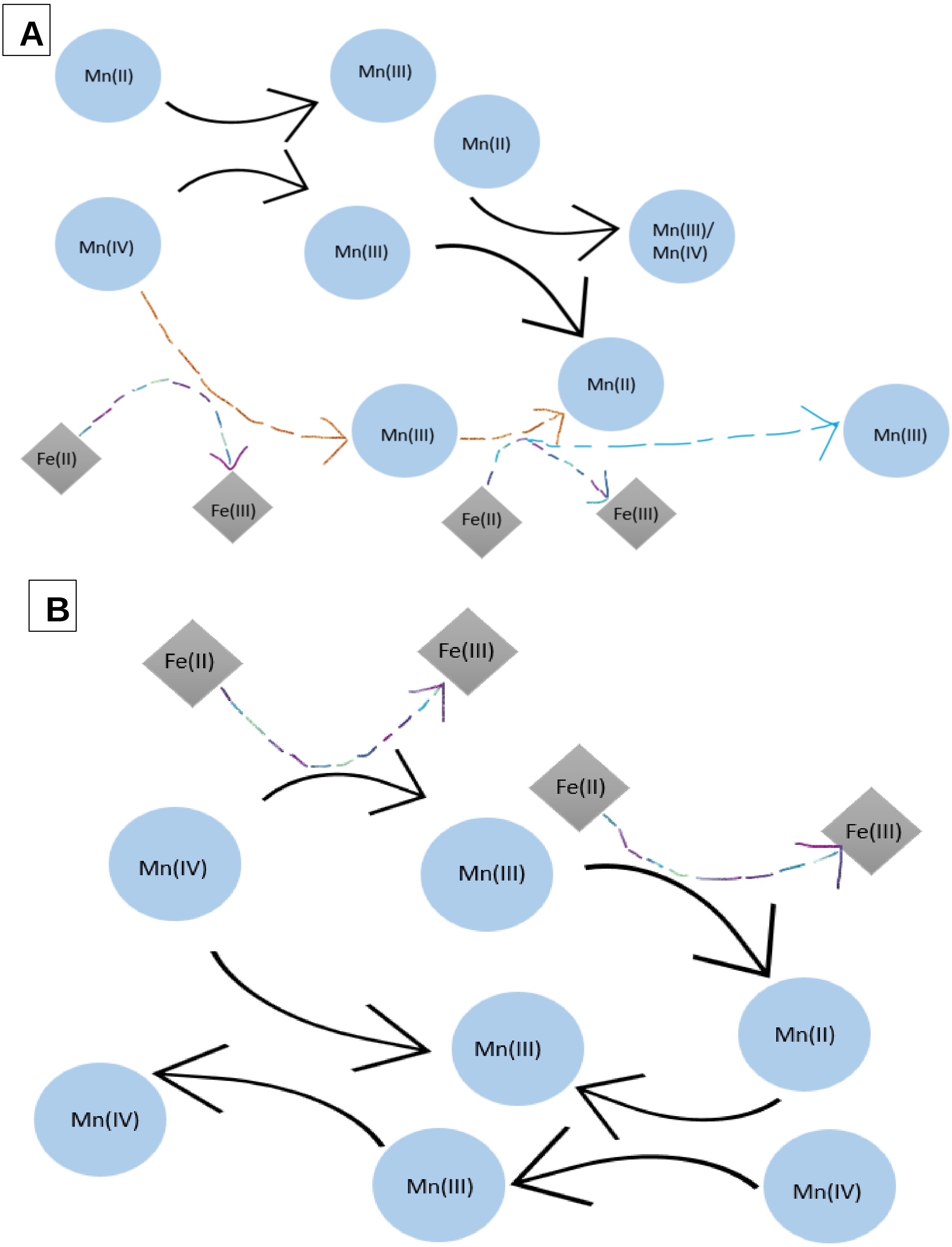


Figure 4.5: Manganese redox interaction flow scheme (A) and (B)

5) Conclusions

Based on the various experiments and the literature review done on the manganese and iron redox and co-oxidation reactions, the following conclusions can be made:

i) Mn(IV) reduction occurs in groundwater filters under both aerobic and anoxic conditions, and it follows the same reduction pathways.

ii) Hypothetically, it is proposed that dissolved Mn was found as a reduction product of MnO_2-Fe(II) system, where Mn(IV) got reduced to Mn(II). Hence, in the presence of dissolved iron, there is mobilization of Mn(II) (higher in anoxic and a lower pH of 6.5).

iii) Moreover, Mn(IV) is not entirely reduced to Mn(II), but a part of it remains in the metastable solid form of Mn(III), which has been theoretically calculated, and it gradually decreases when the Mn(II) mobilization increases.

Also, there was a gap in the experimental dissolved Mn values and the theoretical Mn values, potentially leading to a mismatch in the molar ratios of Fe oxidized: Mn reduced.

Additionally, it can be concluded that manganese can be removed solely by MnO_2 under anoxic conditions, although, under aerobic conditions the removal efficiency is faster with an optimal Mn(II) removal efficiency at pH=7.5.

6) Future Recommendations

Due to the difficulties and challenges faced during the experimentation phase, there were many aspects of the research that remained undiscovered. Therefore, the following future recommendations are advised that can lead to better insights of the research:

i) Redox kinetics at different layers of the filter bed should have been studied.

ii) Working on tools for better comparison of Mn and Fe kinetics under different conditions.

iii) Consideration of both maintaining and destroying the micro-organisms could lead to distinguishing the role of both biotic and abiotic manganese oxidation.

iv) Proper pH maintenance and monitoring is always something that can have an impact on the research to a greater extent.

v) Proper microscopic and macroscopic characterization of the MnO_2 solids both before and after the experiments would lead to better qualitative as well as quantitative analysis of the sorbed manganese species.

vi) Additional experiments to check any possible manganese re-oxidation in the filter that can enhance the overall manganese removal in the system might reduce net manganese release.

vii) Experiments dosing Fe(II), Fe(III), Mn(III), Mn(II), NH_4^+ and PO_4^{3-} under different pH and DO conditions, studying the manganese redox kinetics would allow us to have an overall better picture of all the different manganese oxidation and reduction pathways. Study of the NH_4^+ oxidation, its impact on manganese reduction and an emphasis on the nitrate cycle can also be the next point of focus. Studying the effect of varying MnO_2 concentration in the Mn release kinetics would have also been handy as an additional research.

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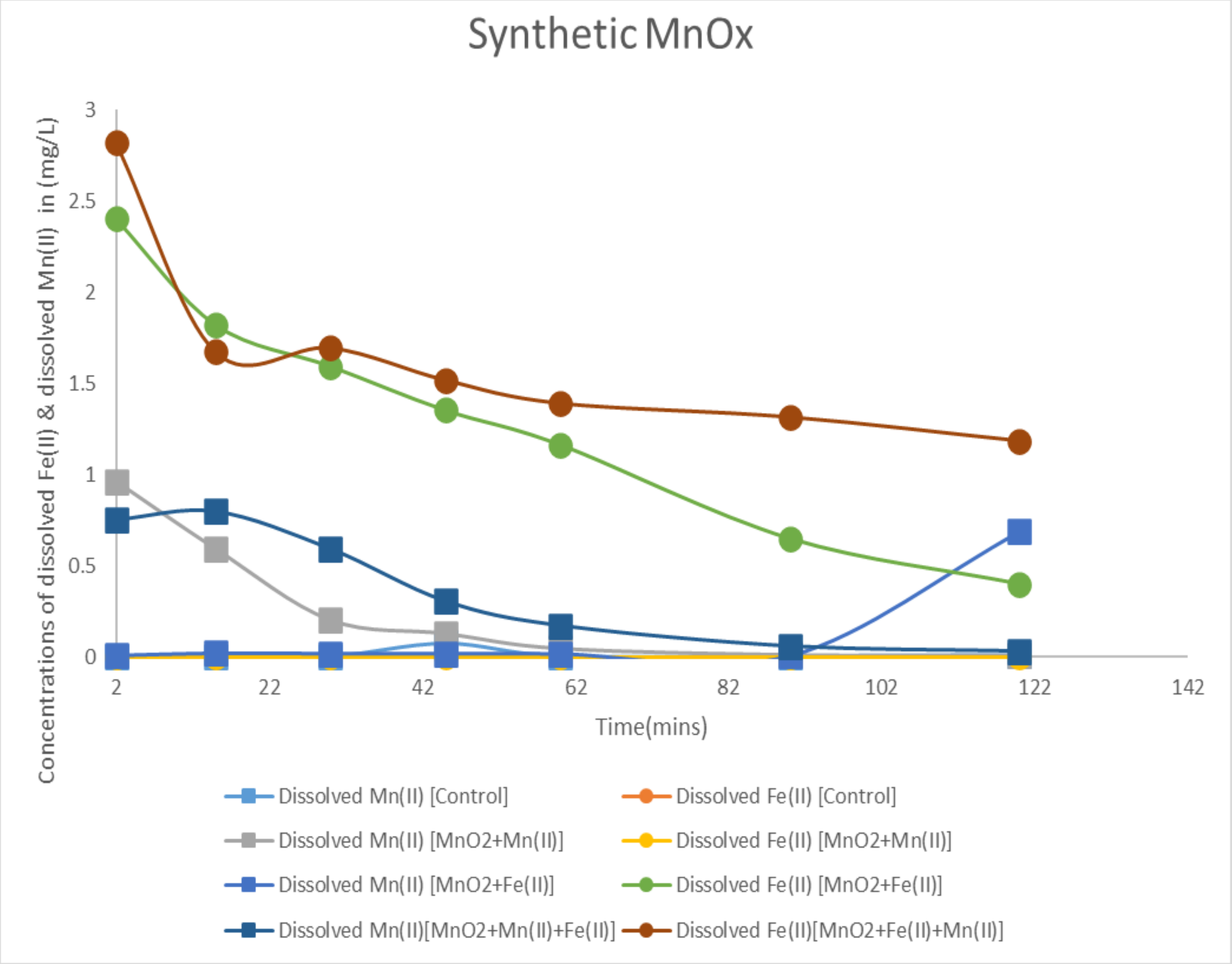
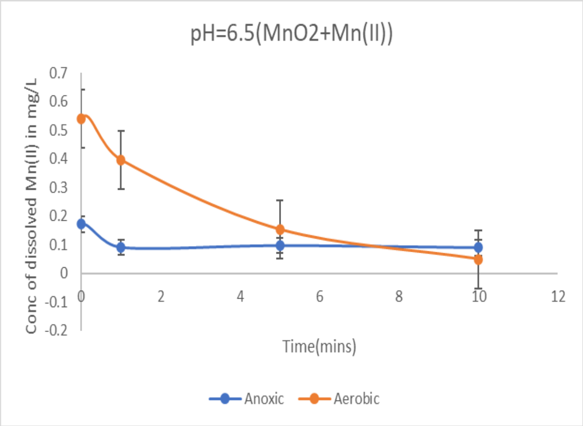
Appendix

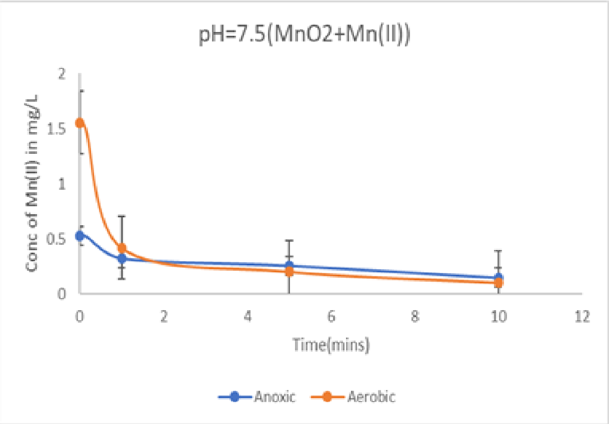
1)



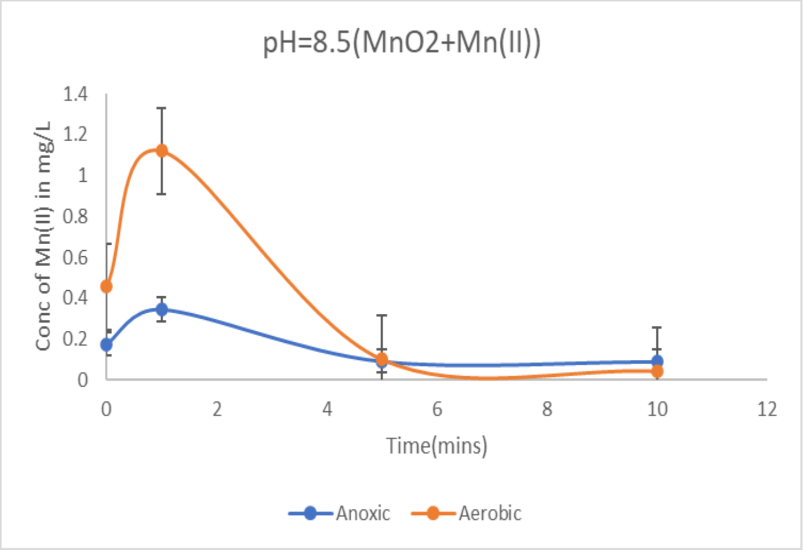
2)A



2)B



2)C



3)

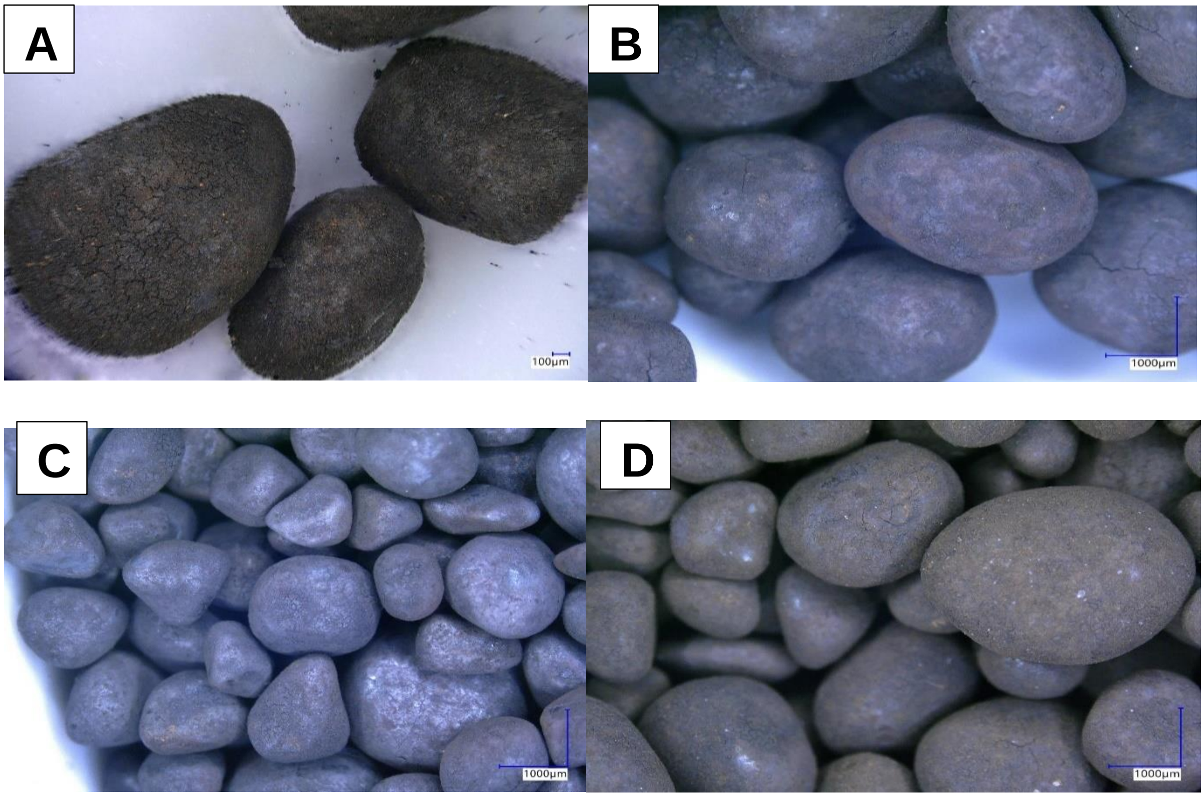
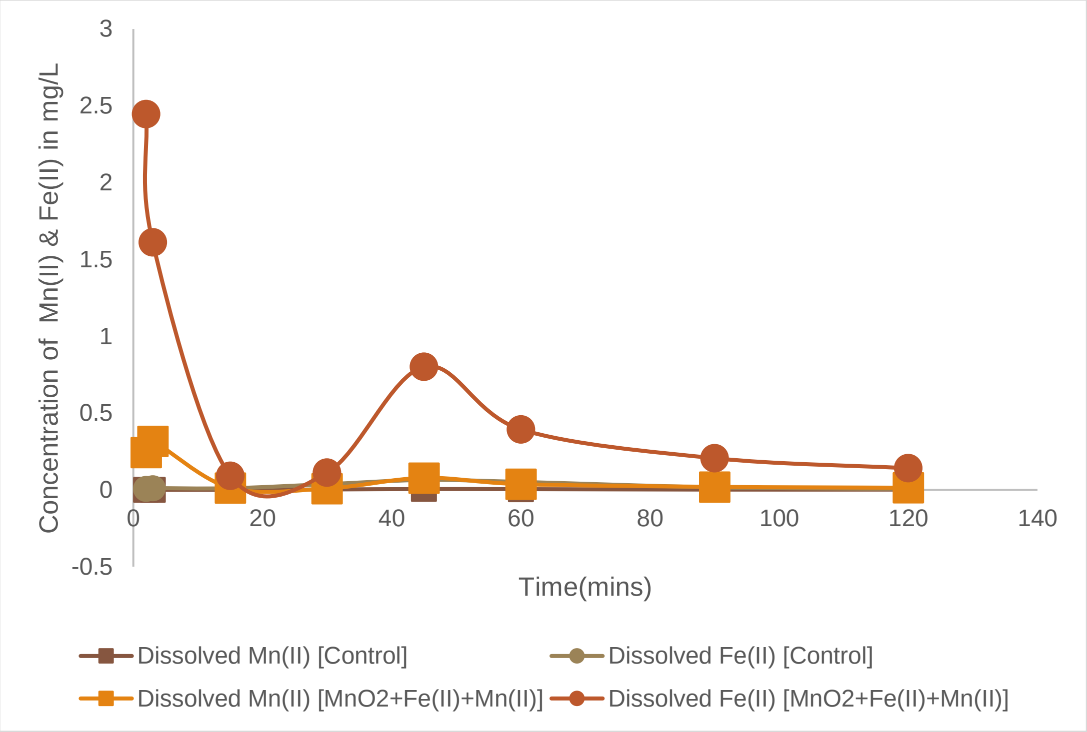
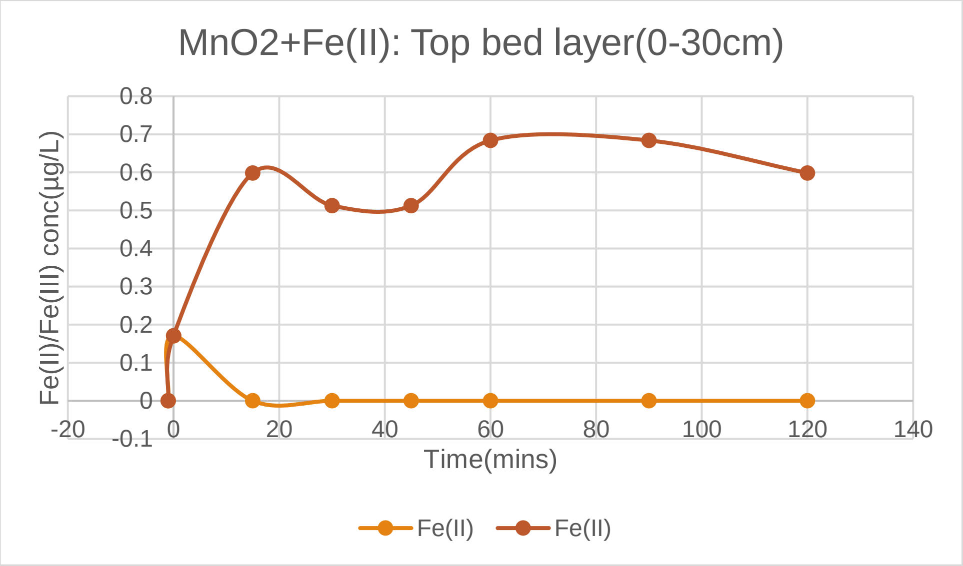


Figure: Microscopic images of the filter media(Vitens, Holten) after experimental run time with A)MnO_2 + Mn(II)=1mg/L at DO=8-9mg/L, B)MnO_2 + Fe(II)=10mg/L at DO=8-9mg/L, C) MnO_2 + Mn(II)=1mg/L at DO=0.0-0.03mg/L,D) MnO_2 + Fe(II)=10mg/L at DO=8-9mg/L.[pH=7.5]

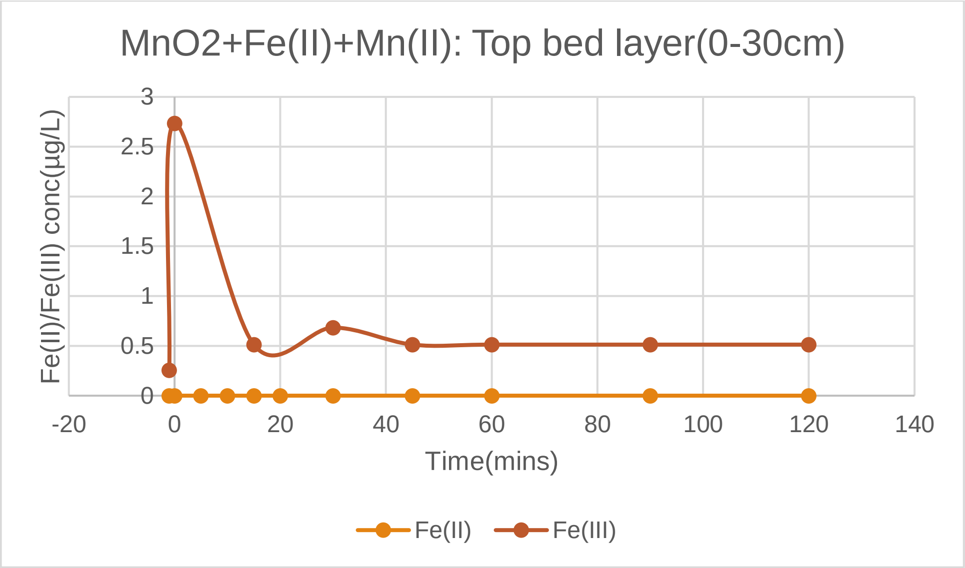
4)


Concentration of Mn(II) & Fe(II) in mg/L
3
2.5
2
1.5
1
0.5
0
-0.5
0
20
40
60
80
100
120
140
Time(mins)
Dissolved Mn(II) [Control]
Dissolved Fe(II) [Control]
Dissolved Mn(II) [MnO2+Fe(II)+Mn(II)]
Dissolved Fe(II) [MnO2+Fe(II)+Mn(II)]

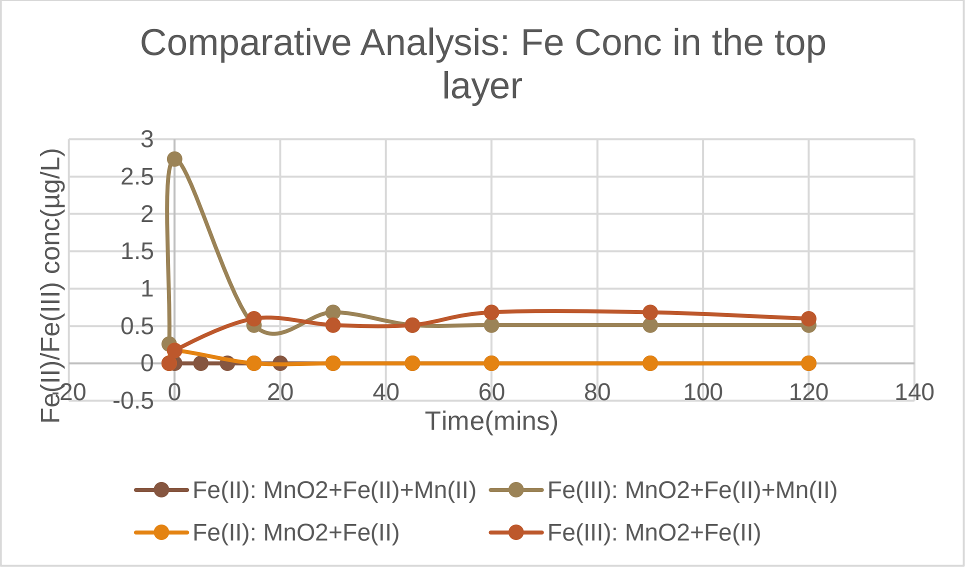
5)


MnO2+Fe(II): Top bed layer(0-30cm)
Fe(II)/Fe(III) conc(µg/L)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe(II)
Fe(II)

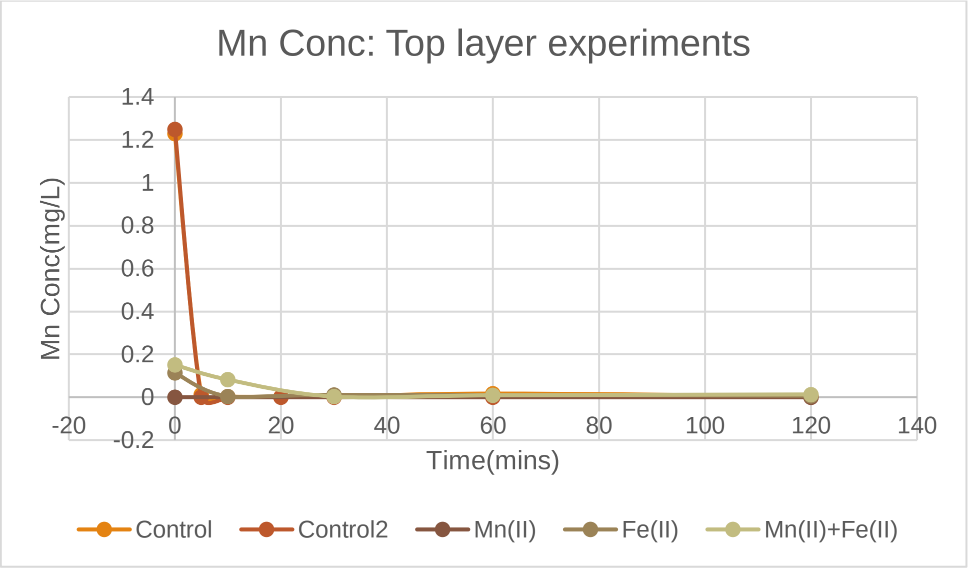
6)


MnO2+Fe(II)+Mn(II): Top bed layer(0-30cm)
Fe(II)/Fe(III) conc(µg/L)
3
2.5
2
1.5
1
0.5
0
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe(II)
Fe(III)

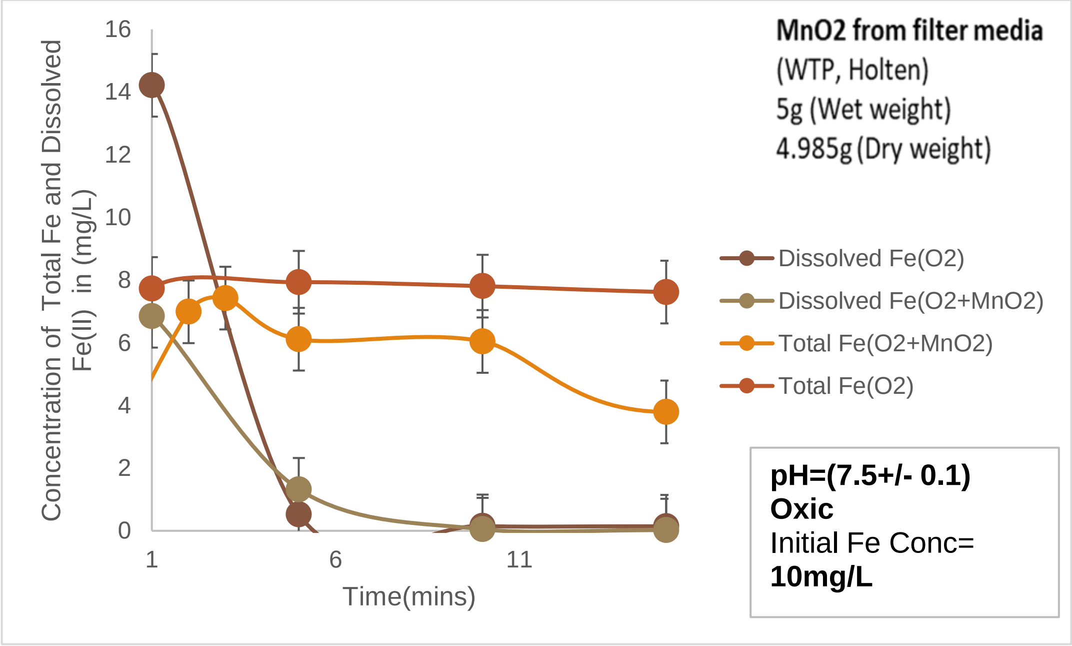
7)


Comparative Analysis: Fe Conc in the top layer
Fe(II)/Fe(III) conc(µg/L)
3
2.5
2
1.5
1
0.5
0
-0.5
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe(II): MnO2+Fe(II)+Mn(II)
Fe(III): MnO2+Fe(II)+Mn(II)
Fe(II): MnO2+Fe(II)
Fe(III): MnO2+Fe(II)

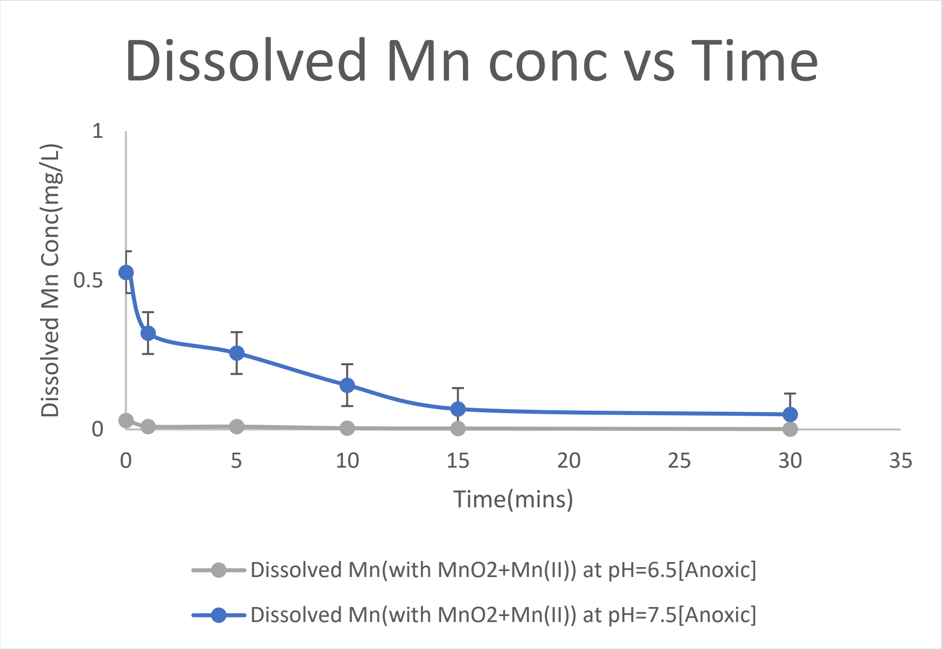
8)


Mn Conc: Top layer experiments
Mn Conc(mg/L)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
-20
0
20
40
60
80
100
120
140
Time(mins)
Control
Control2
Mn(II)
Fe(II)
Mn(II)+Fe(II)

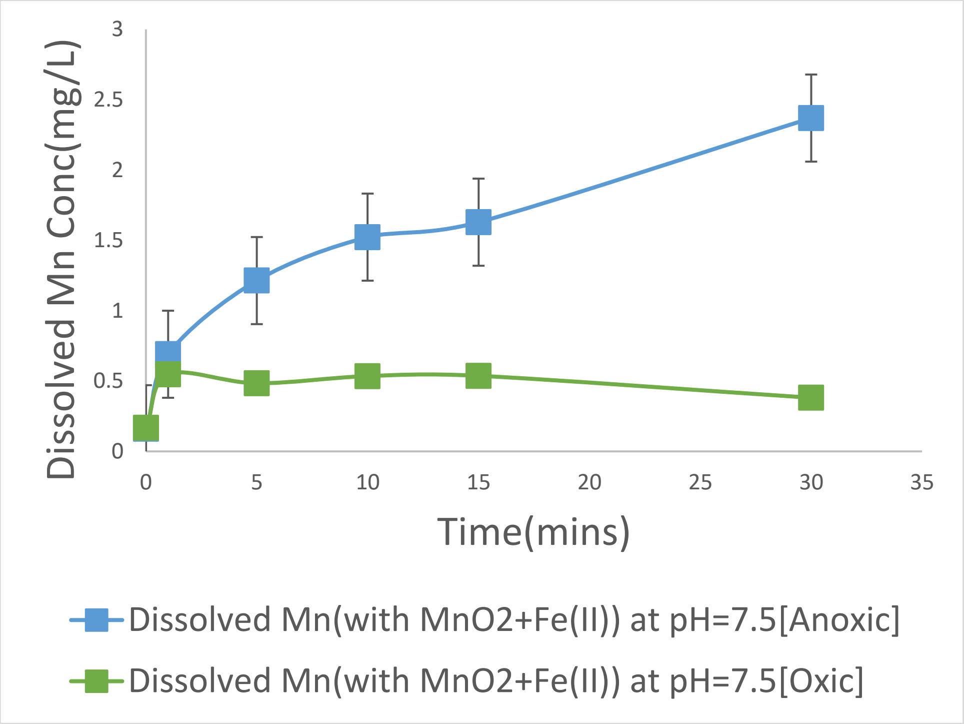
9)


Concentration of Total Fe and Dissolved Fe(II) in (mg/L)
16
14
12
10
8
6
4
2
0
1
6
11
Time(mins)
MnO2 from filter media
(WTP, Holten)
5g (Wet weight)
4.985g (Dry weight)
Dissolved Fe(O2)
Dissolved Fe(O2+MnO2)
Total Fe(O2+MnO2)
Total Fe(O2)
pH=(7.5+/- 0.1)
Oxic
Initial Fe Conc=
10mg/L

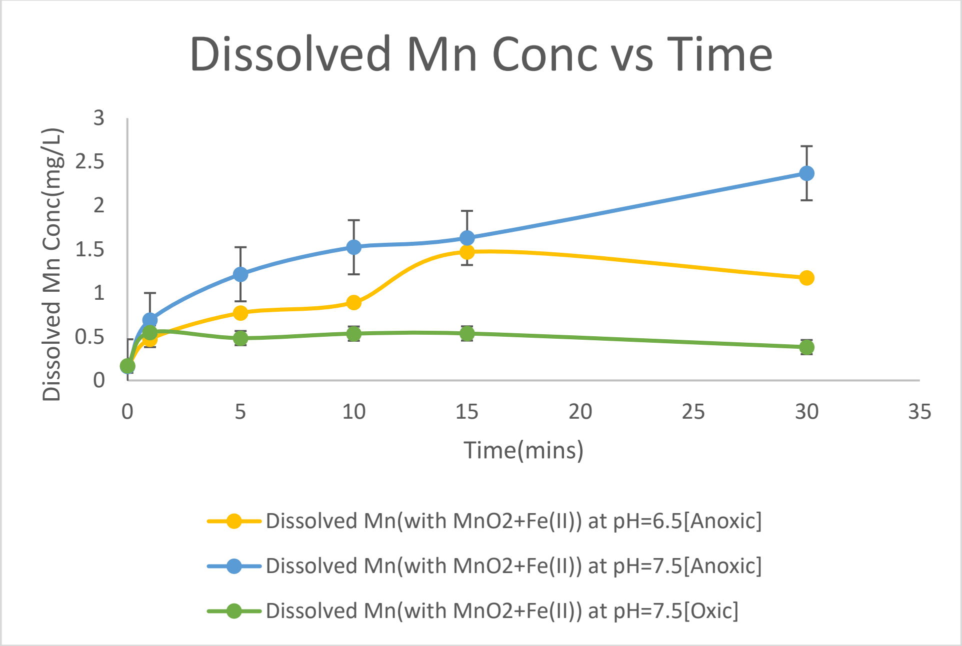
10)


Dissolved Mn conc vs Time
Dissolved Mn Conc(mg/L)
1
0.5
0
0
5
10
15
20
25
30
35
Time(mins)
Dissolved Mn(with MnO2+Mn(II)) at pH=6.5[Anoxic]
Dissolved Mn(with MnO2+Mn(II)) at pH=7.5[Anoxic]

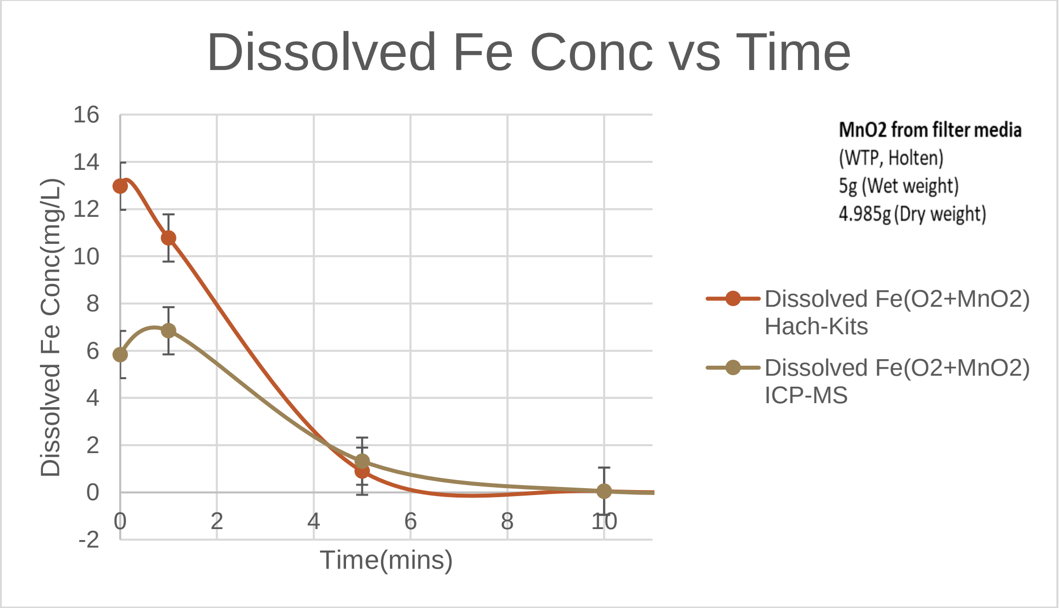
11)


Dissolved Mn Conc(mg/L)
3
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
30
35
Time(mins)
Dissolved Mn(with MnO2+Fe(II)) at pH=7.5[Anoxic]
Dissolved Mn(with MnO2+Fe(II)) at pH=7.5[Oxic]

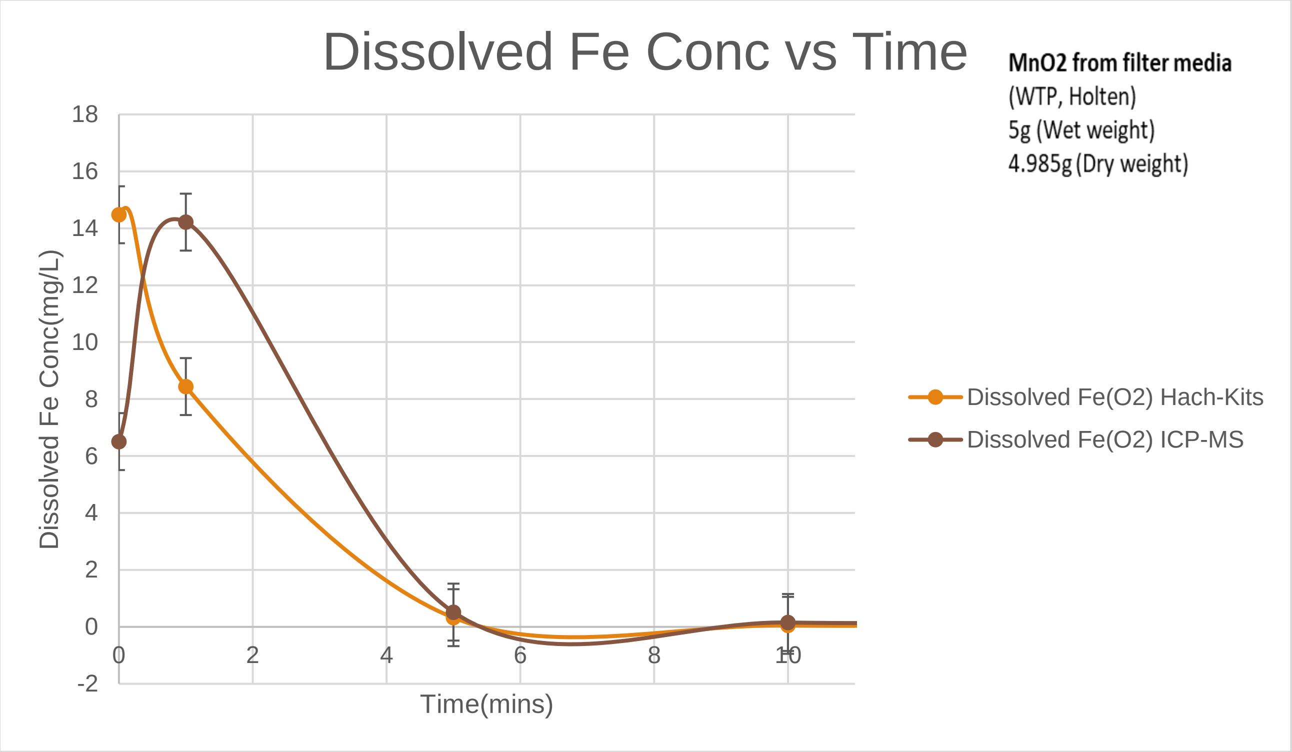
12)


Dissolved Mn Conc vs Time
Dissolved Mn Conc(mg/L)
3
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
30
35
Time(mins)
Dissolved Mn(with MnO2+Fe(II)) at pH=6.5[Anoxic]
Dissolved Mn(with MnO2+Fe(II)) at pH=7.5[Anoxic]
Dissolved Mn(with MnO2+Fe(II)) at pH=7.5[Oxic]

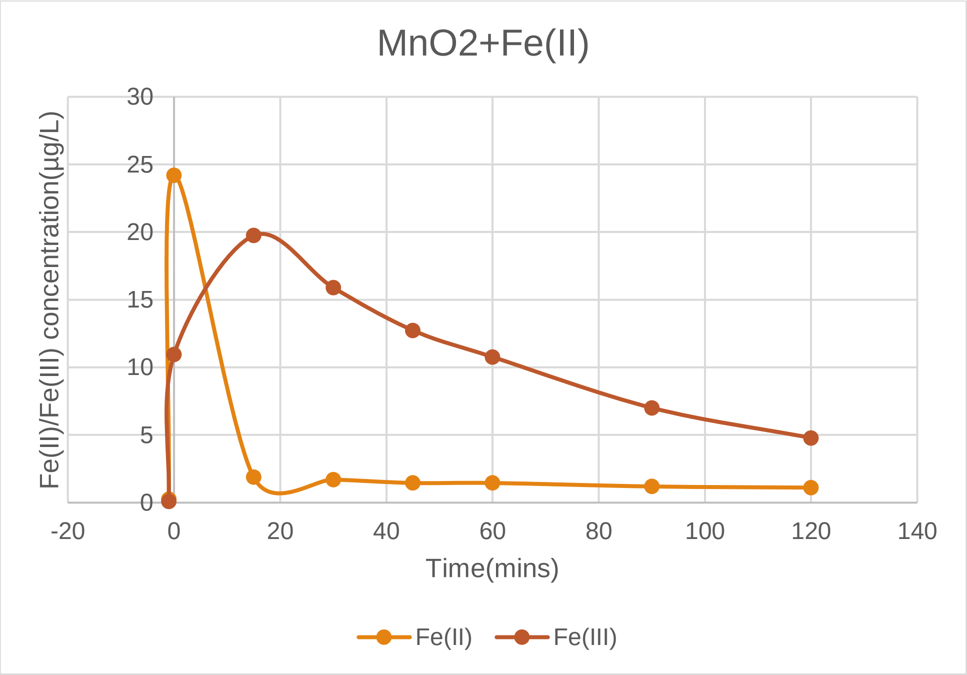
13)


Dissolved Fe Conc vs Time
Dissolved Fe Conc(mg/L)
16
14
12
10
8
6
4
2
0
-2
0
2
4
6
8
10
Time(mins)
MnO2 from filter media
(WTP, Holten)
5g (Wet weight)
4.985g (Dry weight)
Dissolved Fe(O2+MnO2) Hach-Kits
Dissolved Fe(O2+MnO2) ICP-MS

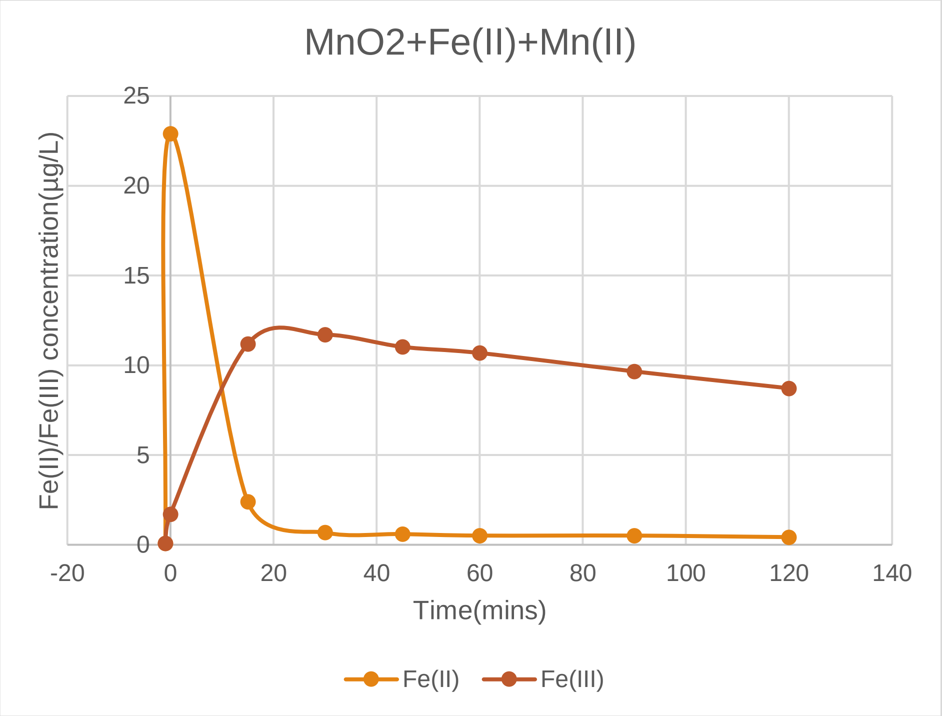
14)


Dissolved Fe Conc vs Time
MnO2 from filter media
(WTP, Holten)
5g (Wet weight)
4.985g (Dry weight)
Dissolved Fe Conc(mg/L)
18
16
14
12
10
8
6
4
2
0
-2
0
2
4
6
8
10
Time(mins)
Dissolved Fe(O2) Hach-Kits
Dissolved Fe(O2) ICP-MS

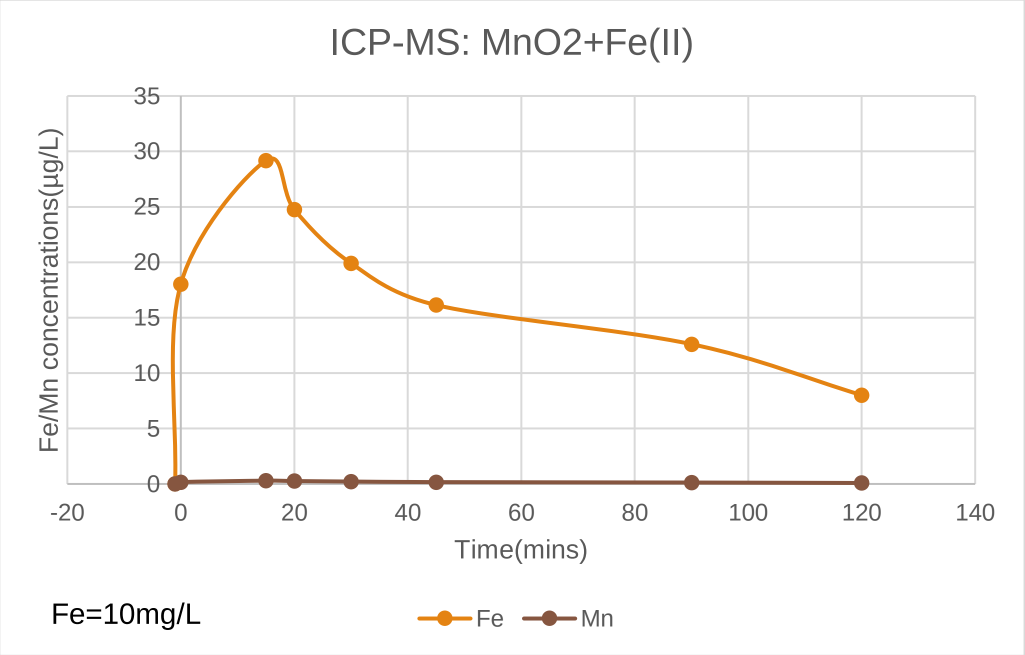
15)


MnO2+Fe(II)
Fe(II)/Fe(III) concentration(µg/L)
30
25
20
15
10
5
0
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe(II)
Fe(III)

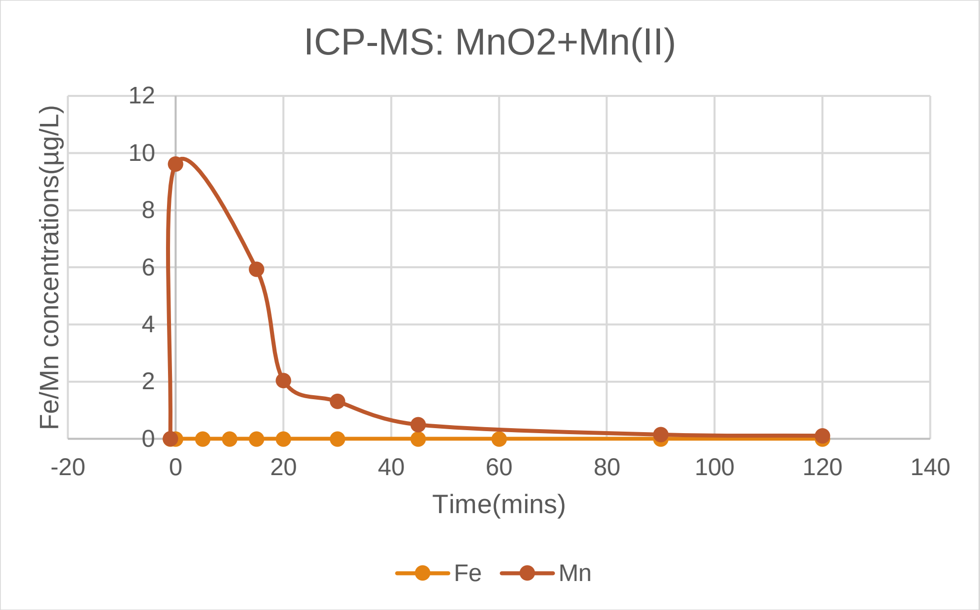
16)


MnO2+Fe(II)+Mn(II)
Fe(II)/Fe(III) concentration(µg/L)
25
20
15
10
5
0
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe(II)
Fe(III)

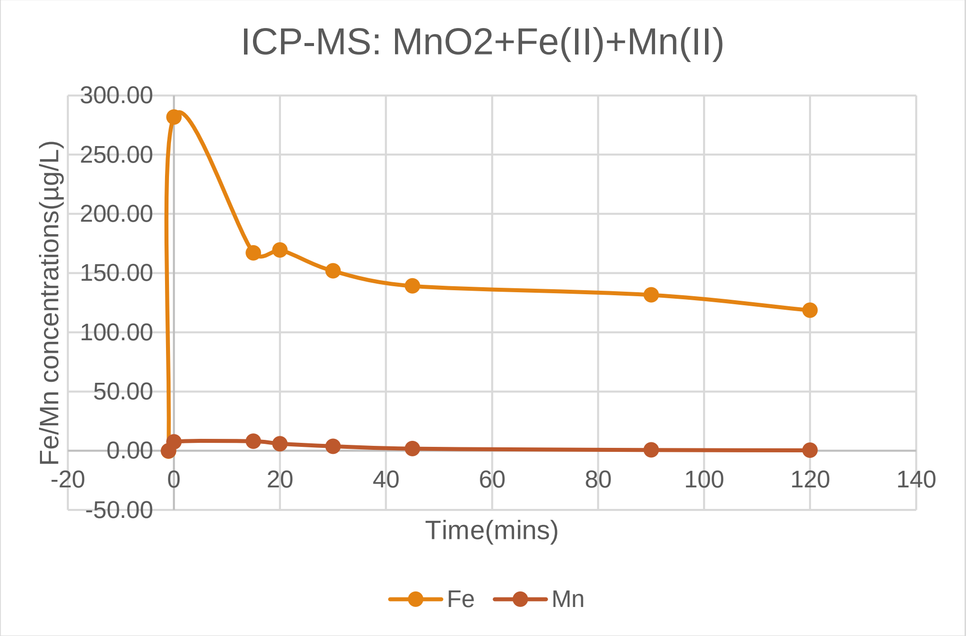
17)


ICP-MS: MnO2+Fe(II)
Fe/Mn concentrations(µg/L)
35
30
25
20
15
10
5
0
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe=10mg/L
Fe
Mn

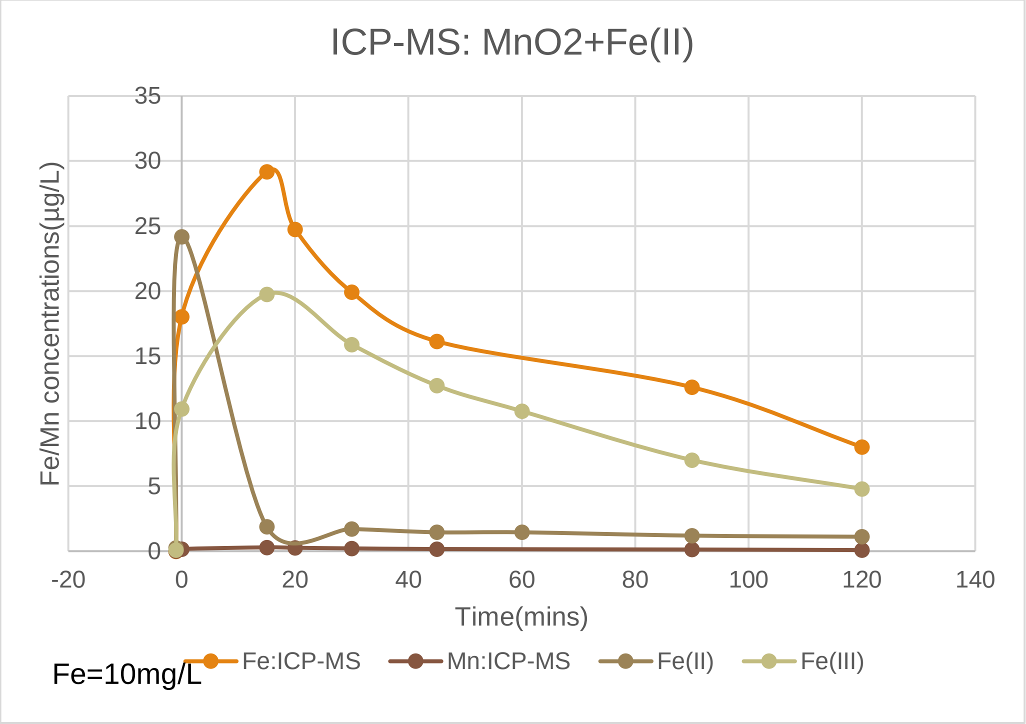
18)


ICP-MS: MnO2+Mn(II)
Fe/Mn concentrations(µg/L)
12
10
8
6
4
2
0
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe
Mn

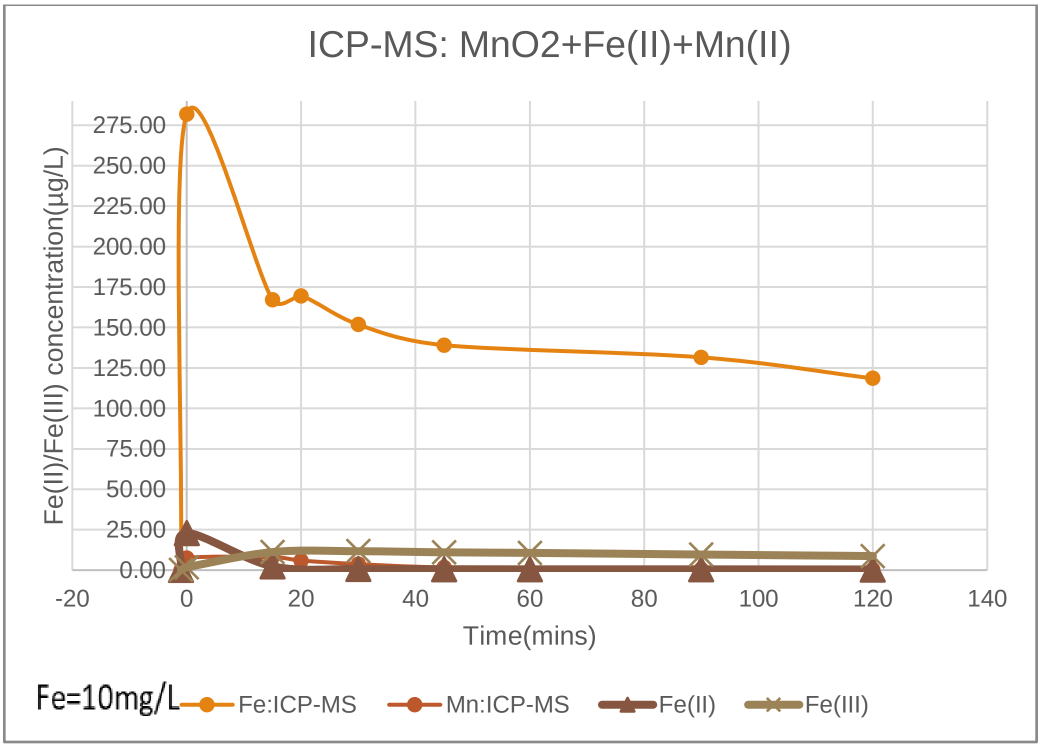
19)


ICP-MS: MnO2+Fe(II)+Mn(II)
Fe/Mn concentrations(µg/L)
300.00
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe
Mn

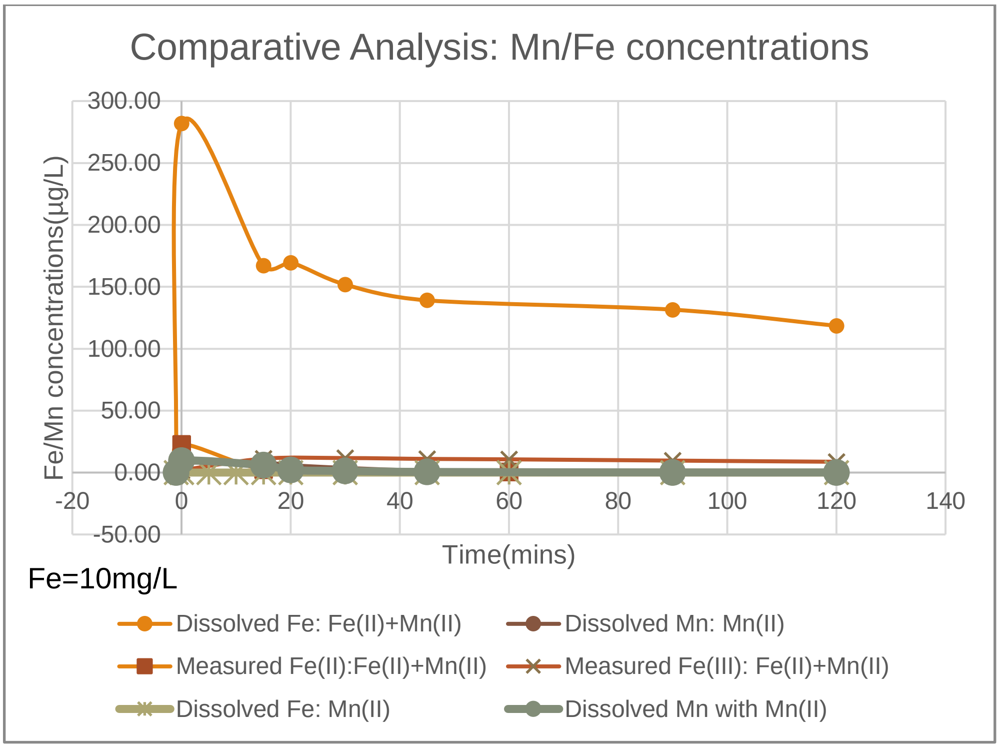
20)


ICP-MS: MnO2+Fe(II)
Fe/Mn concentrations(µg/L)
35
30
25
20
15
10
5
0
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe=10mg/L
Fe:ICP-MS
Mn:ICP-MS
Fe(II)
Fe(III)

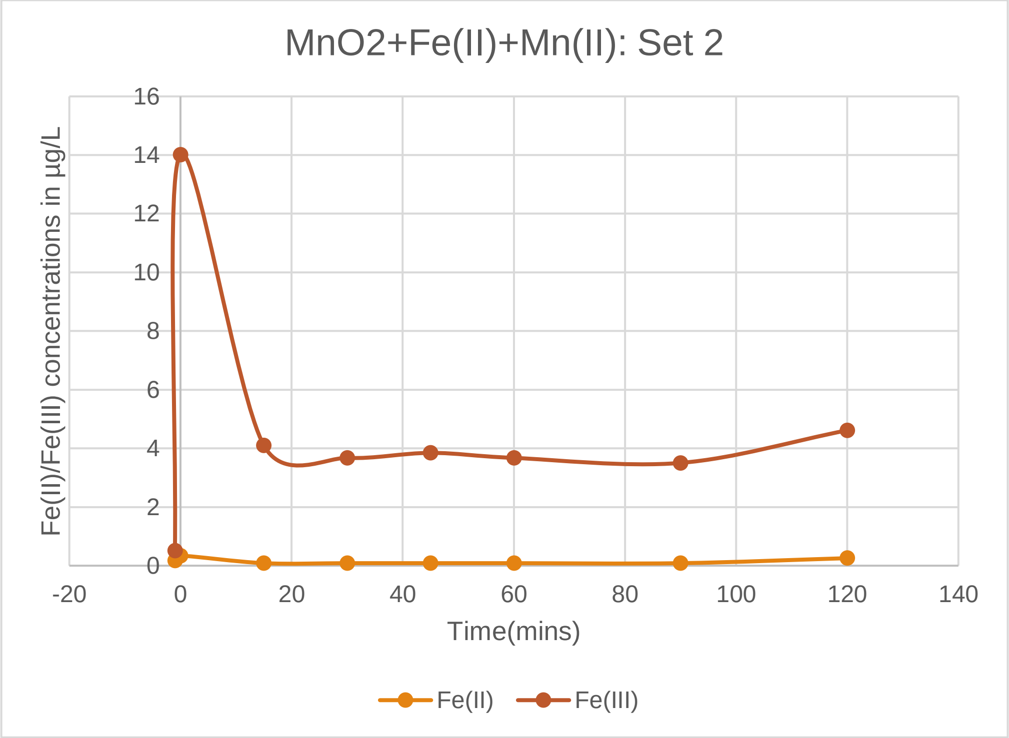
21)


ICP-MS: MnO2+Fe(II)+Mn(II)
Fe(II)/Fe(III) concentration(µg/L)
275.00
250.00
225.00
200.00
175.00
150.00
125.00
100.00
75.00
50.00
25.00
0.00
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe=10mg/L
Fe:ICP-MS
Mn:ICP-MS
Fe(II)
Fe(III)

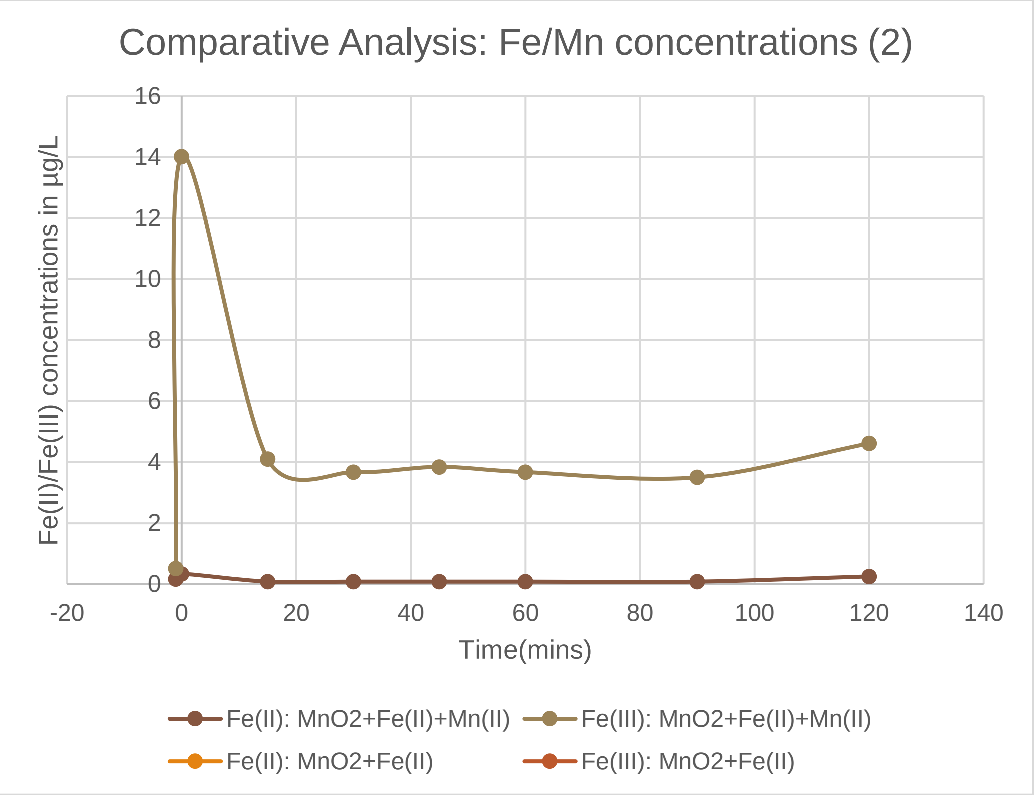
22)


Comparative Analysis: Mn/Fe concentrations
Fe/Mn concentrations(µg/L)
300.00
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe=10mg/L
Dissolved Fe: Fe(II)+Mn(II)
Dissolved Mn: Mn(II)
Measured Fe(II):Fe(II)+Mn(II)
Measured Fe(III): Fe(II)+Mn(II)
Dissolved Fe: Mn(II)
Dissolved Mn with Mn(II)

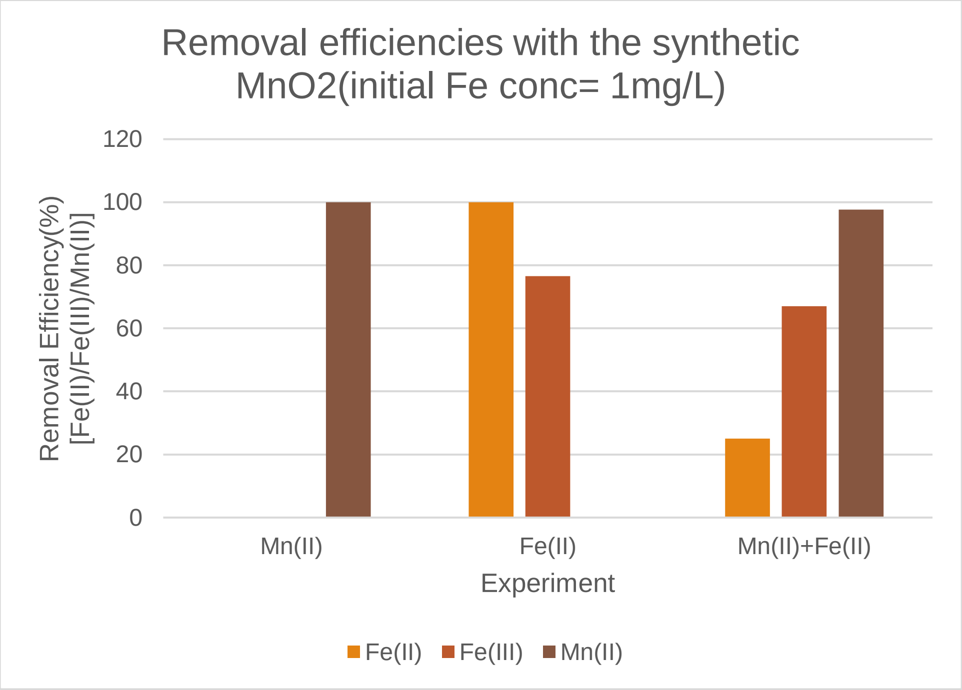
23)


MnO2+Fe(II)+Mn(II): Set 2
Fe(II)/Fe(III) concentrations in µg/L
16
14
12
10
8
6
4
2
0
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe(II)
Fe(III)

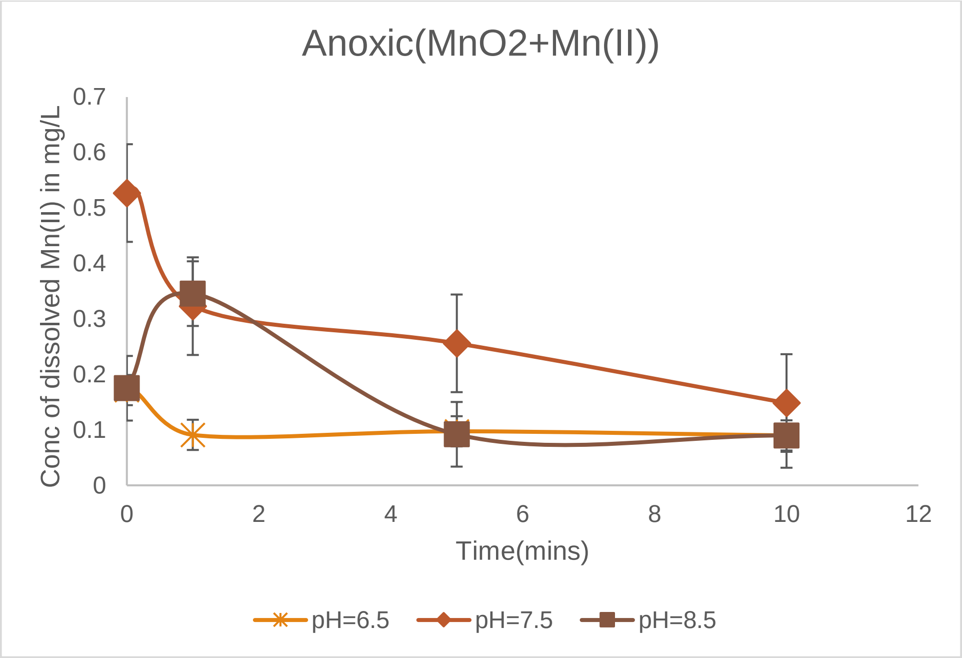
24)


Comparative Analysis: Fe/Mn concentrations (2)
Fe(II)/Fe(III) concentrations in µg/L
16
14
12
10
8
6
4
2
0
-20
0
20
40
60
80
100
120
140
Time(mins)
Fe(II): MnO2+Fe(II)+Mn(II)
Fe(III): MnO2+Fe(II)+Mn(II)
Fe(II): MnO2+Fe(II)
Fe(III): MnO2+Fe(II)

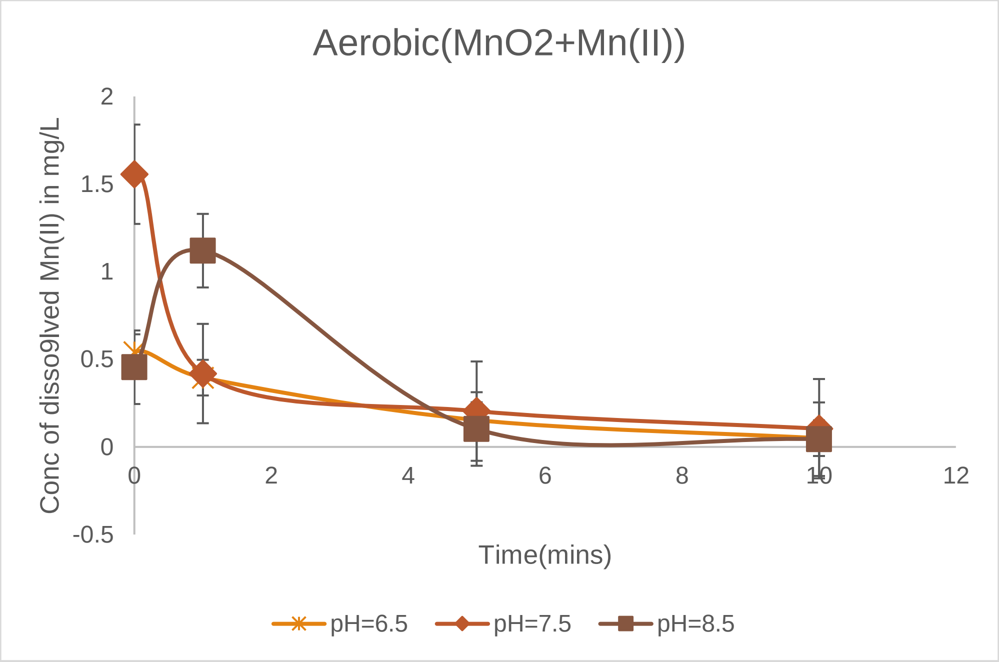
25)


Removal efficiencies with the synthetic MnO2(initial Fe conc= 1mg/L)
Removal Efficiency(%) [Fe(II)/Fe(III)/Mn(II)]
120
100
80
60
40
20
0
Mn(II)
Fe(II)
Mn(II)+Fe(II)
Experiment
Fe(II)
Fe(III)
Mn(II)

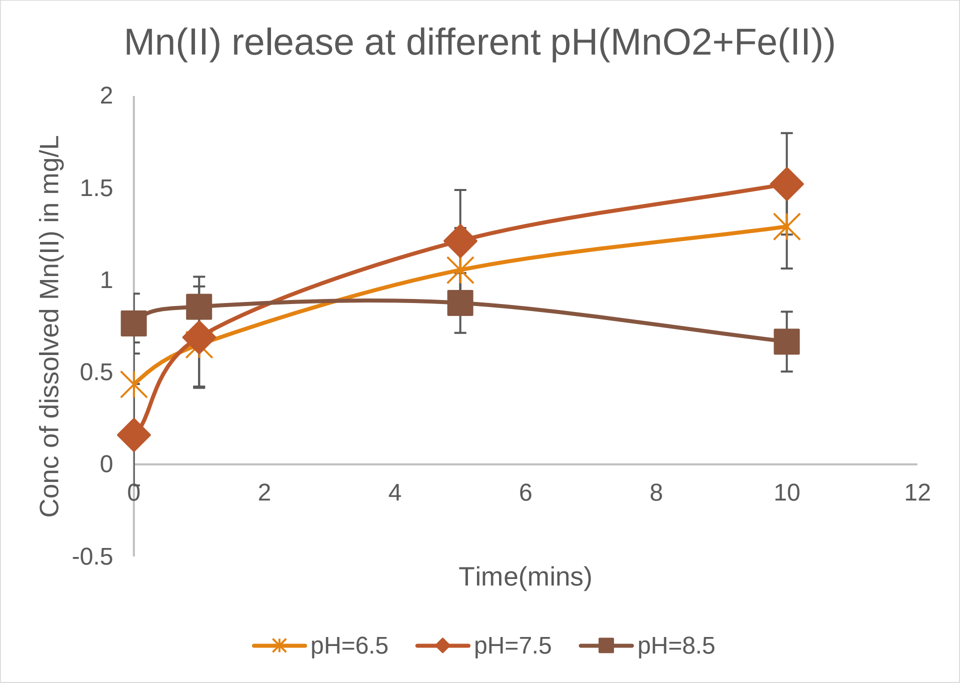
26)


Anoxic(MnO2+Mn(II))
Conc of dissolved Mn(II) in mg/L
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10
12
Time(mins)
pH=6.5
pH=7.5
pH=8.5

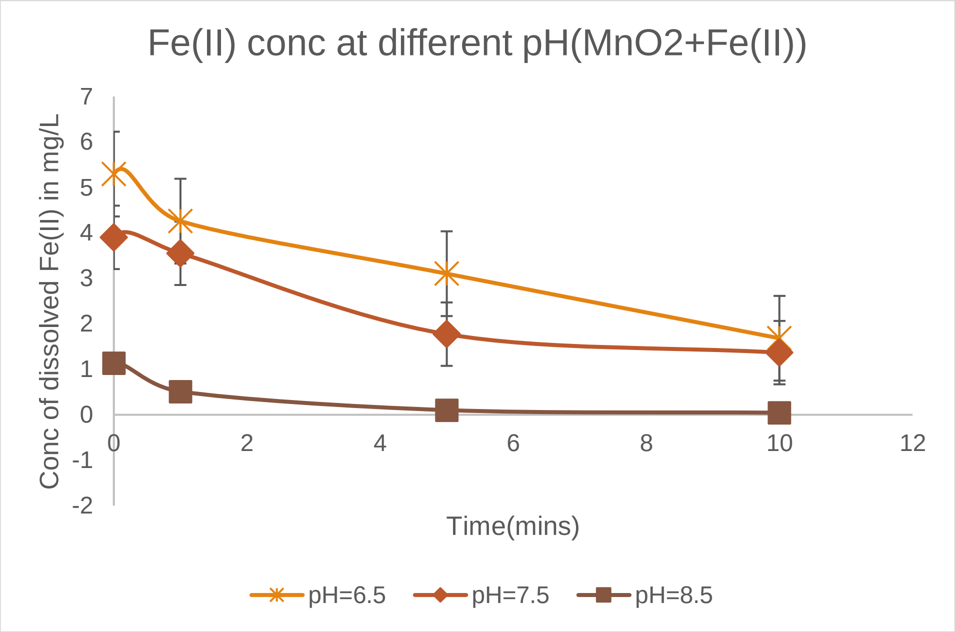
27)


Aerobic(MnO2+Mn(II))
Conc of disso9lved Mn(II) in mg/L
2
1.5
1
0.5
0
-0.5
0
2
4
6
8
10
12
Time(mins)
pH=6.5
pH=7.5
pH=8.5

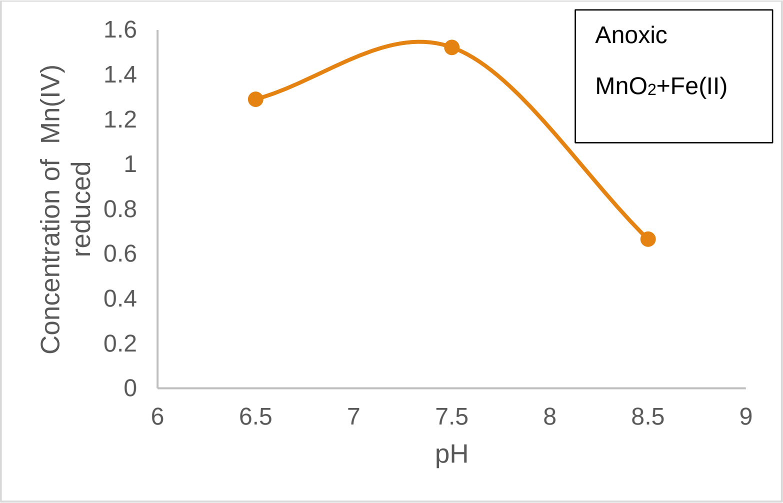
28)


Mn(II) release at different pH(MnO2+Fe(II))
Conc of dissolved Mn(II) in mg/L
2
1.5
1
0.5
0
-0.5
0
2
4
6
8
10
12
Time(mins)
pH=6.5
pH=7.5
pH=8.5

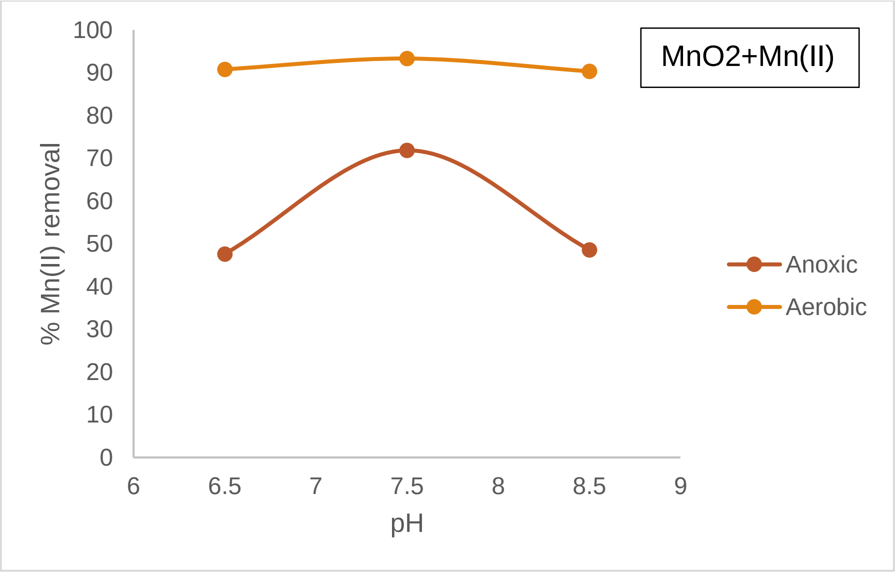
29)


Fe(II) conc at different pH(MnO2+Fe(II))
Conc of dissolved Fe(II) in mg/L
7
6
5
4
3
2
1
0
-1
-2
0
2
4
6
8
10
12
Time(mins)
pH=6.5
pH=7.5
pH=8.5

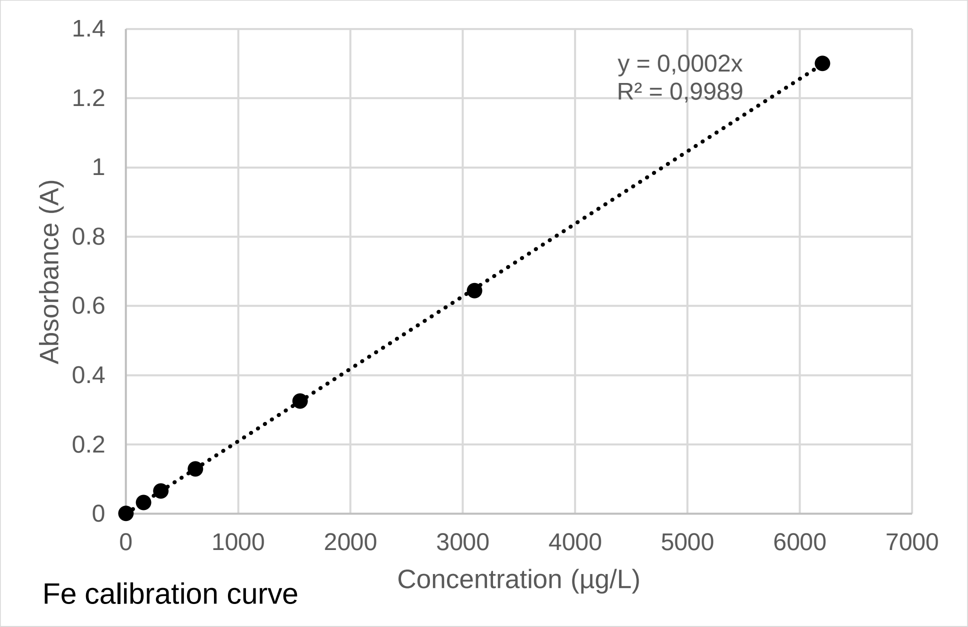
30)


Anoxic
MnO_2+Fe(II)
Concentration of Mn(IV) reduced
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
6
6.5
7
7.5
8
8.5
9
pH

31)

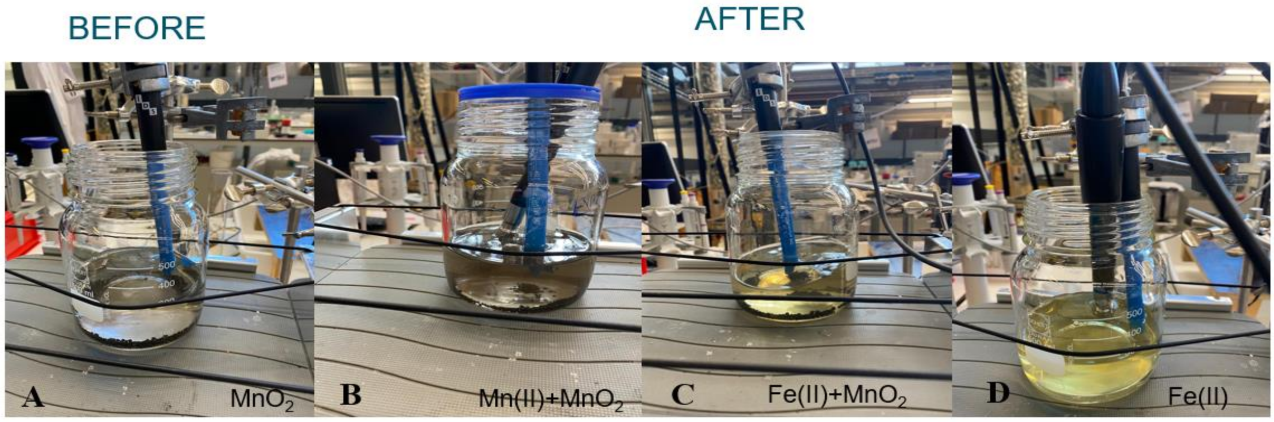

MnO2+Mn(II)
% Mn(II) removal
100
90
80
70
60
50
40
30
20
10
0
6
6.5
7
7.5
8
8.5
9
pH
Anoxic
Aerobic

32)



Fe calibration curve

33) Aerobic



34) Anoxic

35)

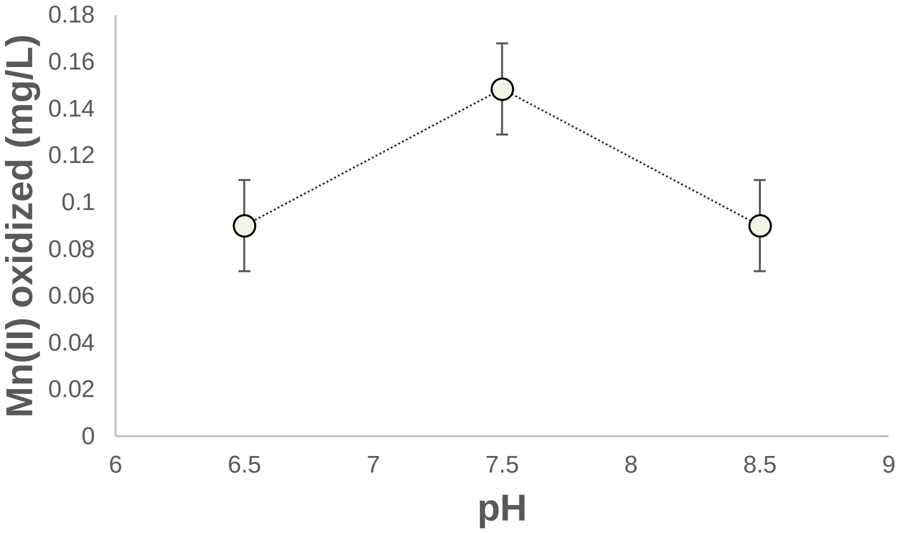


Figure : Concentration of the measured dissolved manganese oxidized at different pH = 6.5, 7.5 and 8.5 in the experiments with MnO_2+Mn(II) system involving 20g/L MnO_2 (Holten filter media) and 1mg/L dosed Mn(II) for 10 minutes [DO=0.0-0.03 mg/L]

36)

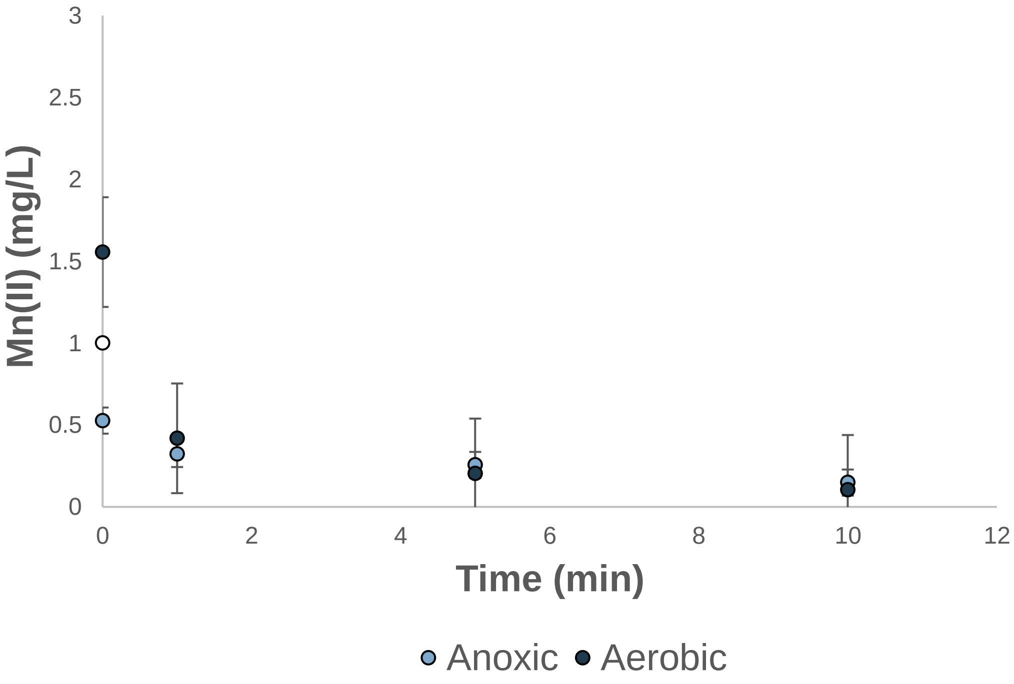


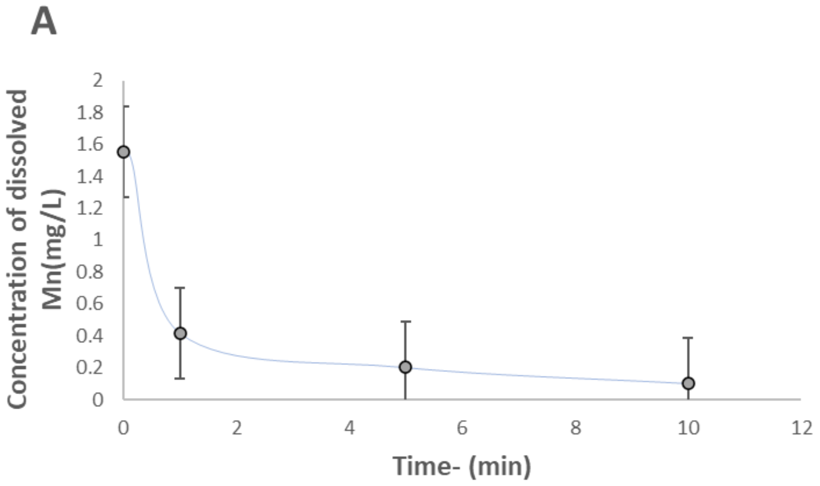
Figure : Concentration of the measured dissolved manganese oxidized under anoxic [DO = 8-9mg/L] and aerobic [DO = 0.0-0.03 mg/L] conditions in the experiments with MnO_2+Mn(II) system involving 20g/L MnO_2 (Holten filter media)and 1mg/L dosed Mn(II) with respect to run time in minutes [pH=7.5]

37)

Table: Operational parameters for initial experiments

Experiment	MnOx	Dissolved Mn	Dissolved Fe	NH4
Control	40 g/L	-	-	0.5 mg N/L
Mn	40 g/L	1 mg/L	-	0.5 mg N/L
Fe	40 g/L	-	1 mg/L	0.5 mg N/L
Mn+Fe (set 1)	40 g/L	1 mg/L	1 mg/L	0.5 mg N/L
Mn+Fe (set 2)	20 g/L	1 mg/L	10 mg/L	0.5 mg N/L

38)



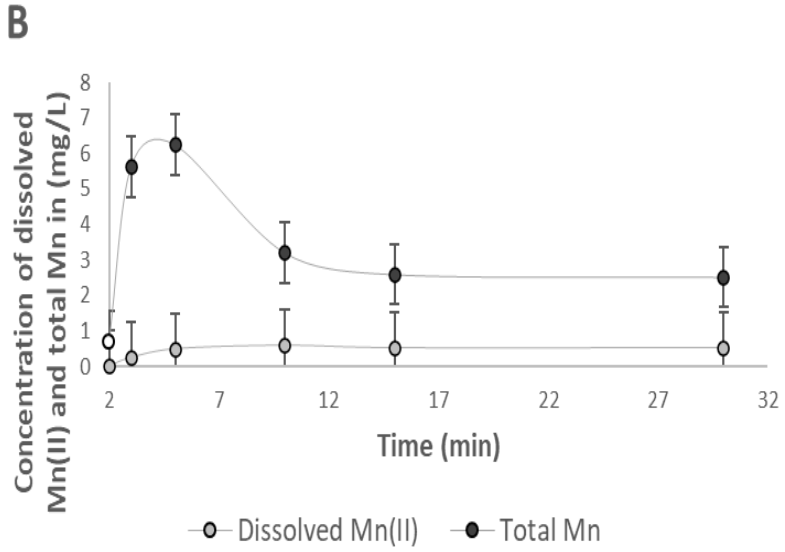


Figure: A) The concentration of dissolved Mn(II) with experiments involving 20g/L MnO_2 and 1mg/L dosed Mn(II), B) the concentration of dissolved Mn(II) & total Mn with experiments involving

39)

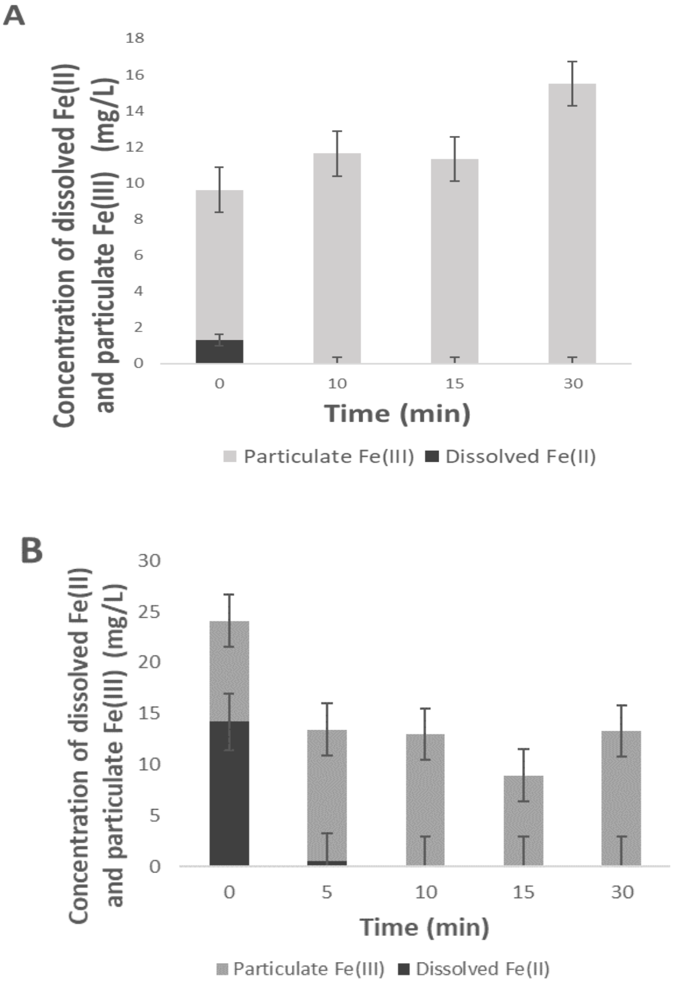


Figure: A) The concentration of dissolved Fe(II) & particulate Fe(III) with experiments involving 20g/L MnO_2(Holten filter media) and 10mg/L dosed Fe(II), B) the concentration of dissolved Fe(II) & particulate Fe(III) with experiments involving only 10mg/L dosed Fe(II) with respect to run time in minutes.[pH=7.5,DO=8-9mg/L]

40)

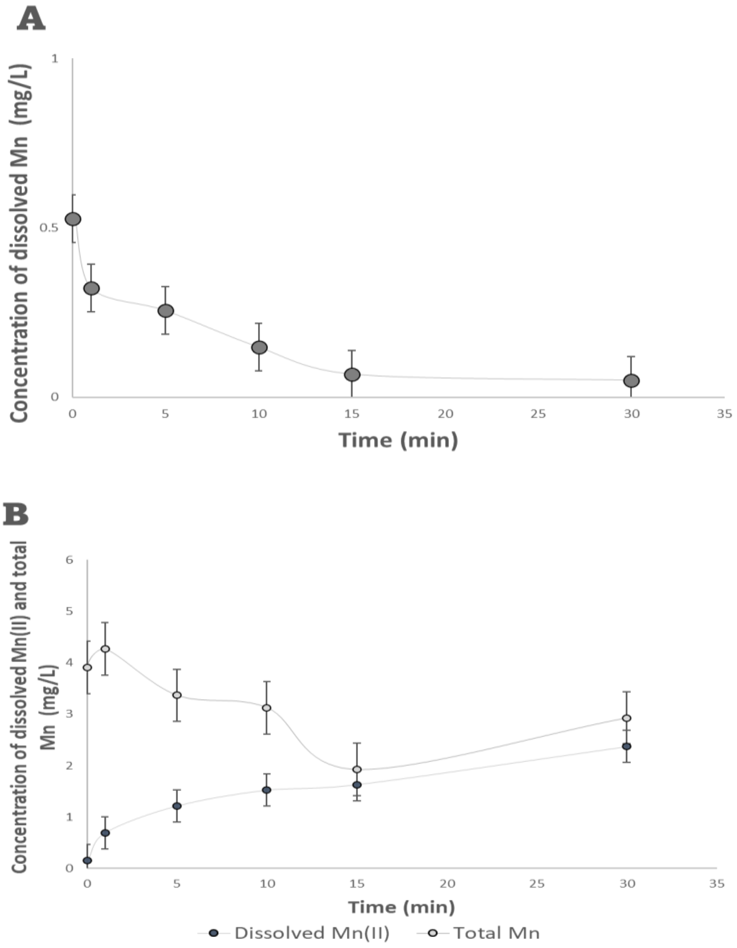


Figure : A) The concentration of dissolved Mn(II) with experiments involving 20g/L MnO_2 and 1mg/L dosed Mn(II), B) the concentration of dissolved Mn(II) & total Mn with experiments involving 20g/L MnO_2 and 10mg/L dosed Fe(II) with respect to run time in minutes and the Holten filter media. [pH=7.5,DO=0.0-0.03 mg/L]

41)

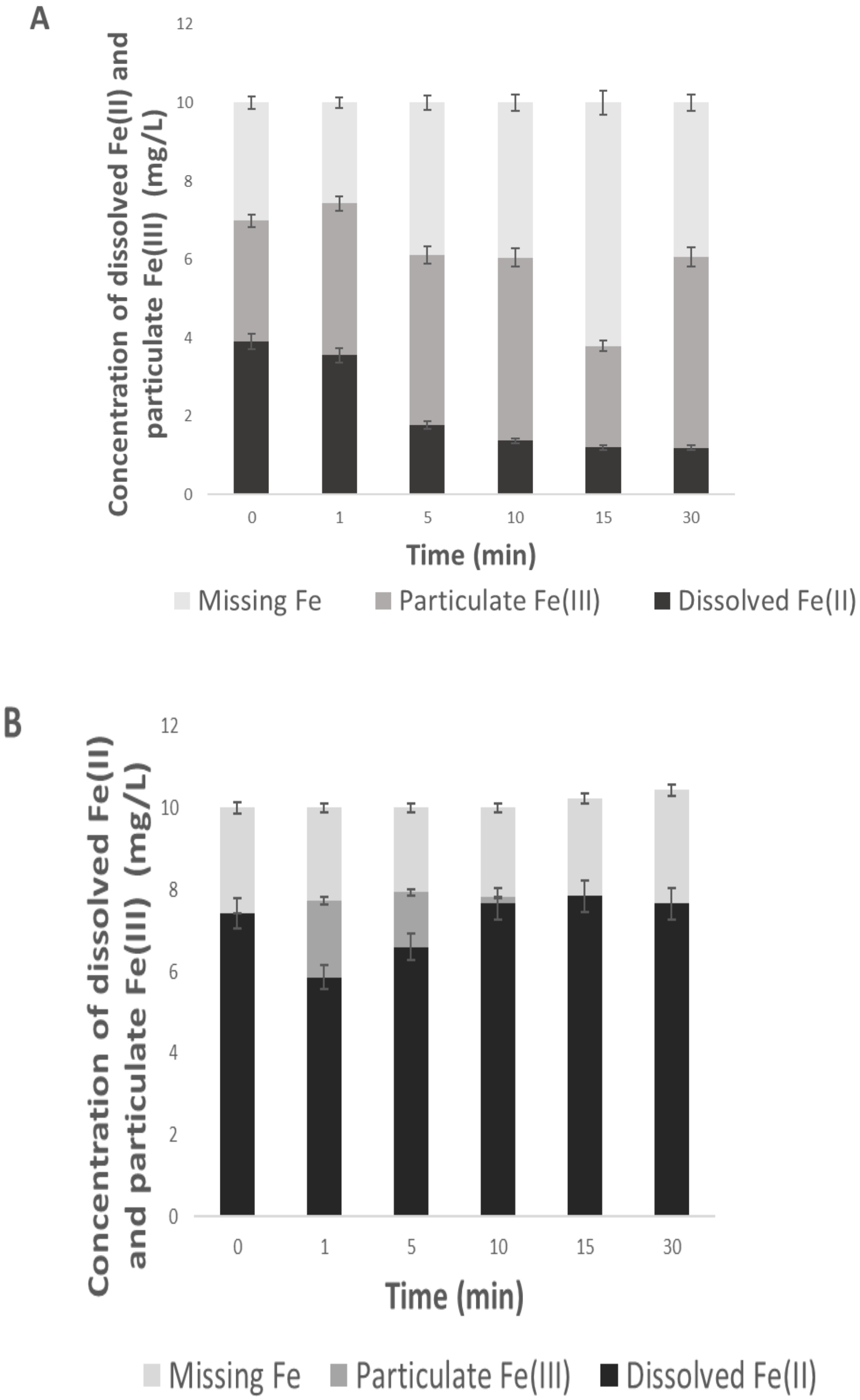


Figure : A) The concentration of dissolved Fe(II), particulate Fe(III) and missing Fe with experiments involving 20g/L MnO_2(Holten filter media) and 10mg/L dosed Fe(II), B) the concentration of dissolved Fe(II), particulate Fe(III) and missing Fe with experiments involving only 10mg/L dosed Fe(II) with respect to run time in minutes.[pH=7.5,DO=0.0-0.03mg/L]

42)

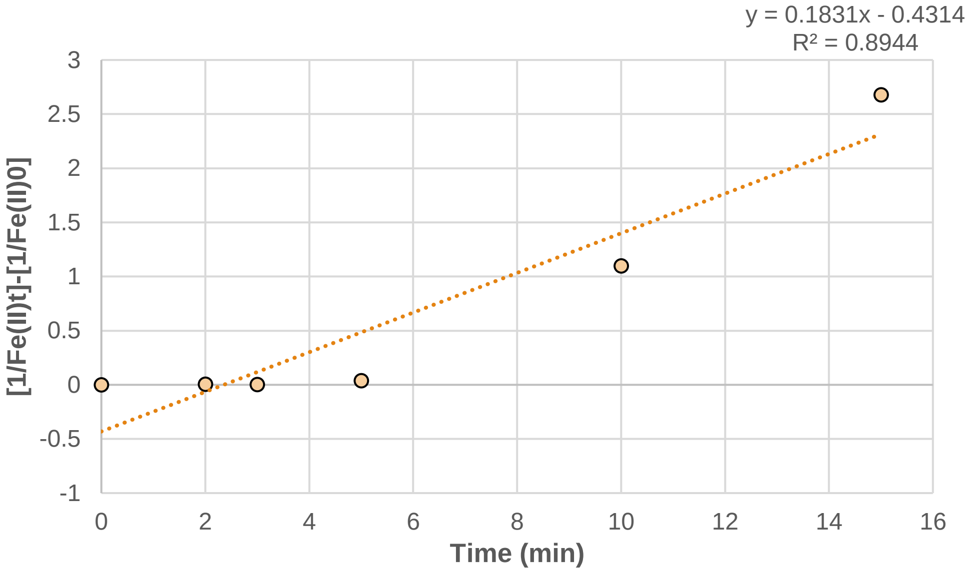


Figure: Kinetics for Fe(II) oxidation under aerobic [DO = 0.0-0.03 mg/L] conditions in MnO_2+Fe(II) system involving 20g/L MnO_2 (Holten filter media) and 10 mg/L dosed Fe(II) [pH=7.5]

43)

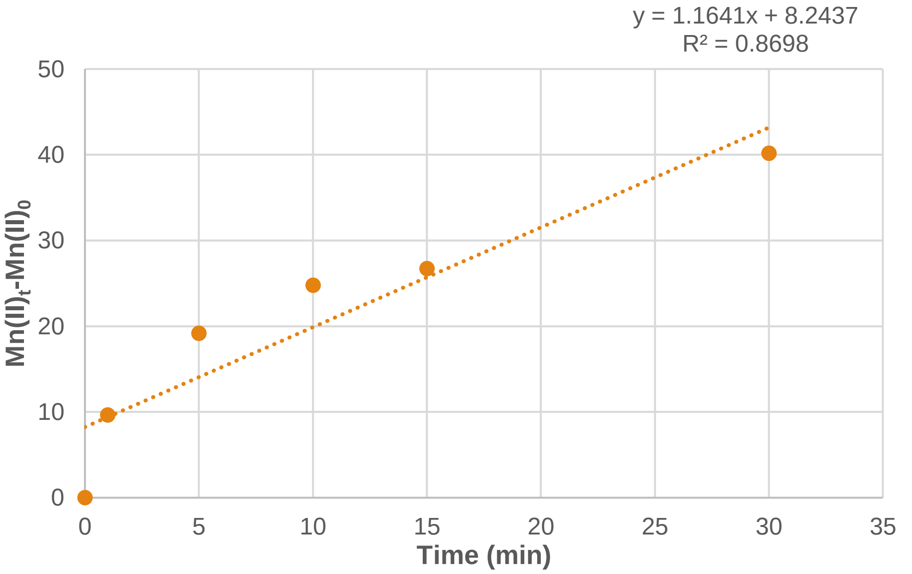


Figure: Kinetics for Mn(II) reduction under anoxic [DO = 0.00-0.03mg/L] conditions in MnO_2+Fe(II) system involving 20g/L MnO_2 (Holten filter media) and 10 mg/L dosed Fe(II) [pH=7.5]

44)

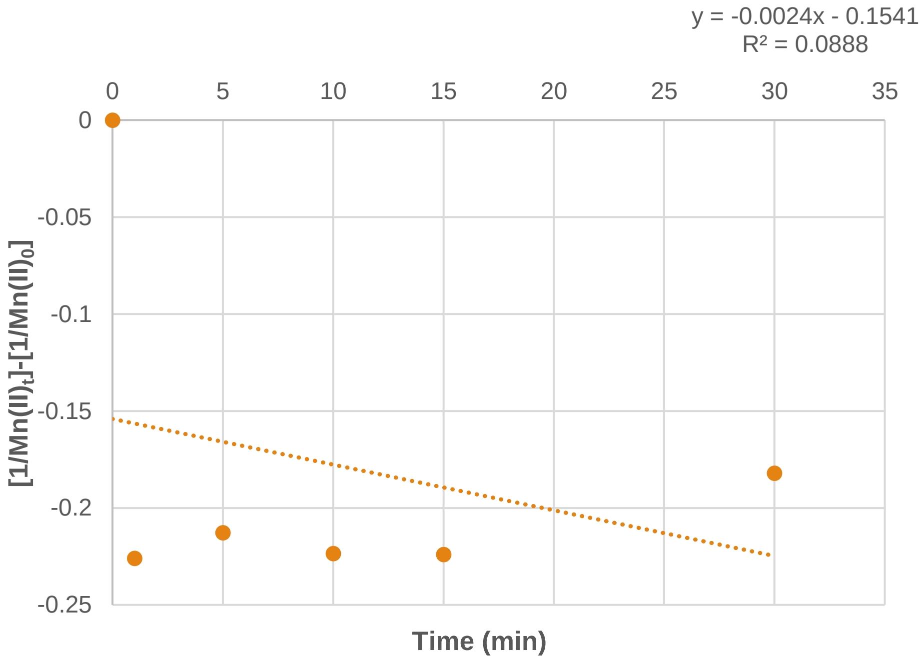


Figure: Kinetics for Mn(II) reduction under aerobic [DO = 8-9mg/L] conditions in MnO_2+Fe(II) system involving 20g/L MnO_2 (Holten filter media) and 10 mg/L dosed Fe(II) [pH=7.5]

45)

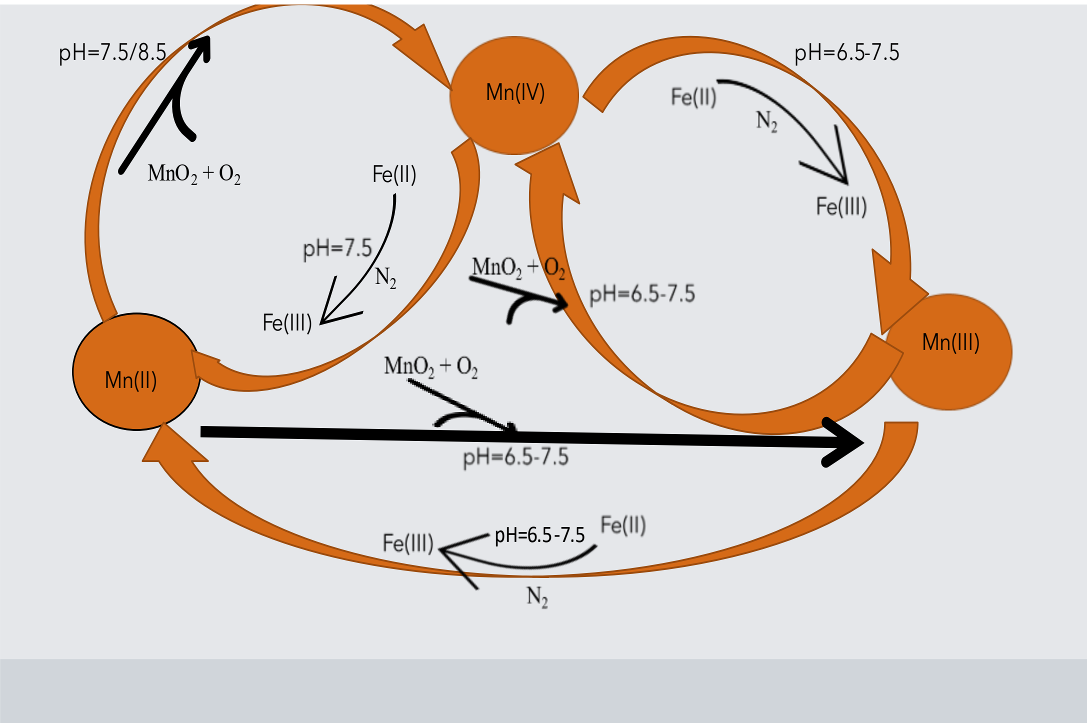


Figure : Descriptive overall manganese redox pathways based on different conditions