



**KTH Land and Water
Resources Engineering**

THE APPLICATION OF MnO_2 AND $KMnO_4$ FOR PERSISTENT ORGANIC COMPOUNDS AND COD REMOVALS IN WASTEWATER TREATMENT PROCESS

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SUMMARY

Water reuse technologies have been employed in different parts of the world to put up with the challenges of regional water scarcity. Water scarcity is global challenge that will get more intense in the coming years as the population increases, world's economy grows, water quality degrades along with increasing demands, and precipitation pattern alters due to climate change. Moreover, the challenge is amplified as wastewater and water treatment industries have been facing challenges since 1990s when increasing amount of Pharmaceutical and Personal Care Product (PPCP) and Endocrine Disruptor Compound (EDC) traces in natural aquatic environments have been detected. These compounds have been deemed as the cause of various alterations in water ecosystem such as the decreased fertility and gender alteration of birds, fish, and mammals. These changes raise a concern that they may have chronic health effect on humans following water consumption over a long period of time. Several treatment technologies, such as membrane (ultrafiltration and reverse osmosis), activated carbon, advanced oxidation process and ozone have been proven effective in retaining these compounds. However, the implementation of these technologies is expensive. This paper is to explore the potential of chemical process by manganese dioxide (MnO₂) and potassium permanganate (KMnO₄) as strong oxidants to remove organic materials in wastewater. Other than its catalytic property, MnO₂ is postulated to be able to oxidize, split, and also adsorb organic compounds. KMnO₄ being a strong oxidant may oxidize and split longer chain molecules into more readily biodegradable ones while it is also being reduced to other manganese species with lower oxidation states (Mn⁶⁺, Mn⁵⁺, Mn⁴⁺, Mn³⁺) that can further oxidize more organic compounds. According to literature studies, both MnO₂ and KMnO₄ can effectively remove phenolic compounds and that their oxidation potential is directly related to pH (low pH is necessary for complete reduction of these manganese compounds to Mn²⁺). KMnO₄ is a stronger oxidant than MnO₂ that can increase the biodegradability of persistent organic compounds. MnO₂ has regenerative property and the presence of other metal ions inhibits the oxidation process by MnO₂. The result from laboratory experiment shows that at pH 8, KMnO₄ is better applied to wastewater that contains low concentration of suspended solids because otherwise, KMnO₄ would break down and solubilize particulate organic materials and add soluble COD concentration. MnO₂ on the other hand, can effectively remove COD without solubilizing particulate organic materials. KMnO₄ application in a stirred reactor can be mixed with the presence of other flocculants and may enhance the oxidation potential of KMnO₄ itself and the overall flocculation process.

SUMMARY IN SWEDISH

Vattenåteranvändningsteknik har använts i olika delar av världen för att möta utmaningar som regional vattenbrist. Vattenbrist som är en global utmaning som kommer att få ökad uppmärksamhet under kommande år som befolkningen ökar och världsekonomin växer, försämrar vattenkvaliteten tillsammans med ökande efterfrågan och förändrade nederbördsmonster på grund av klimatförändringar. Dessutom förstärks utmaningen av att avlopps- och vattenreningsindustrin står inför utmaningar sedan 1990-talet när allt större mängder farmaceutiska och hälsovårdsprodukter (PPCP) och hormonstörande ämnen (EDC) kan spåras i naturliga vattenmiljöer. Dessa föreningar har bedömts som orsak till olika förändringar i vattnets ekosystem, såsom minskad fertilitet och ändring av kön hos fåglar, fiskar och däggdjur. Dessa förändringar tar upp problemet om de kan ha kroniska effekter på människor efter vattenförbrukning under lång tid. Flera behandlingstekniker, såsom membran (ultrafiltrering och omvänd osmos), aktivt kol, avancerad oxidation och ozon har visat sig effektivt i att avlägsna dessa föreningar. Dock är användning av dessa tekniker dyrt. Denna uppsats har som syfte att undersöka potentialen för kemiska processen med mangandioxid (MnO_2) och kaliumpermanganat (KMnO_4) som starka oxidanter för att avlägsna organiskt material i avloppsvatten. Utöver den katalytiska effekten bör MnO_2 kunna oxidera, splittra, och även adsorbera organiska föreningar. KMnO_4 är en stark oxidant som kan oxidera och dela längre kedjemolekyler till mer lättnedbrytbara ämnen medan den samtidigt reduceras till lägre oxidationsstadium (Mn^{6+} , Mn^{5+} , Mn^{4+} , Mn^{3+}) som kan oxidera ytterligare mer organiska föreningar. Enligt litteraturstudier kan både MnO_2 och KMnO_4 effektivt avlägsna fenolföreningar och deras oxidationspotential är direkt relaterad till pH (lågt pH är nödvändig för fullständig reduktion av dessa manganföreningar till Mn^{2+}). KMnO_4 är ett starkare oxidationsmedel än MnO_2 som kan öka den biologiska nedbrytbarheten av långlivade organiska föreningar. MnO_2 har regenerativa egenskaper och förekomsten av andra metalljoner hämmar oxidationen av MnO_2 . Resultatet från laboratorieexperiment visar att vid pH 8 är KMnO_4 bättre användbart på avloppsvatten som innehåller låga koncentrationer av suspenderade ämnen för annars skulle KMnO_4 bryta ner och lösa upp partikulärt organiskt material samt öka koncentrationen löst COD. MnO_2 å andra sidan kan effektivt ta bort COD utan upplösning av partikelbundet organiskt material. Användning av KMnO_4 i ett omrörd reaktor kan blandas med förekomsten av andra flockningsmedel och kan påverka oxidationspotentialen för KMnO_4 och den övergripande flockningsprocessen.

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The application of MnO_2 and KMnO_4 for persistent organic compounds and COD removals
in wastewater treatment process

ABSTRACT

This study examines the use of MnO₂ and KMnO₄ as strong oxidants to remove specific recalcitrant organic compounds and COD from wastewater. These compounds are deemed as potential and more cost-effective treatment in encountering the challenge to remove Pharmaceuticals and Personal Care Products (PPCPs) and Endocrine Disrupter Compounds (EDCs) in wastewater to meet water reuse standard. The literature reviews concluded that both MnO₂ and KMnO₄ were able to remove recalcitrant organic compounds, such as 17 α -ethynylestradiol (EE2), Bisphenol A (BPA), triclosan, and dye wastewater. Simple bench scale experiments were performed to investigate COD removal by utilizing MnO₂ and KMnO₄ to oxidize sewage water and supernatant in a continuously stirred tank reactor at the wastewaters' natural pH (about pH 8). The results indicated that MnO₂ was effective in removing COD of wastewater and not affected by the high content of suspended solids. The effectiveness of KMnO₄ in removing COD of wastewater was masked by its ability to break down and solubilize particulate organic compounds. MnO₂ application could not be mixed with the presence of other metal ions (or flocculants) as their presence may inhibit the efficiency of MnO₂ oxidation. On the other hand, KMnO₄ oxidation efficiency was not affected and even was enhanced by the presence of magnesium and calcium ions as flocculants.

Key words: COD, KMnO₄, MnO₂, Oxidation, Organic compounds

1. INTRODUCTION

This study examines the use of MnO₂ and KMnO₄ as strong oxidants to remove organic compounds in wastewater. These manganese compounds are deemed as potential and more cost-effective treatment in encountering the challenge to remove Pharmaceuticals and Personal Care Products (PPCPs) and Endocrine Disrupter Compounds (EDCs) from wastewater to meet water reuse standard.

1.1. Background and justification of study

Water reuse technologies have been employed in different parts of the world to put up with the challenges of regional water scarcity. Water scarcity is global challenge that will get more intense in the coming years as the population increases, world's economy grows, water quality degrades along with increasing demands, and precipitation pattern alters due to climate change. UN-Water (2007) projects that the world's population will increase from its current status of 6.5 billion to 8.9 billion people by 2050. Meanwhile, in the last century alone, the rate of water use has grown more than twice of the population growth rate. By 2025, UN-Water estimates 1.8 billion people will live with absolute water scarcity, while about 2/3 of the world will live in water stressed areas.

The projections of water scarcity in the future stress the importance and the need to utilize water reuse technologies in wider areas of the world. More urgently, to accommodate the livelihood of the growing populations, more water reuse technologies must meet the standards of potable use. Fortunately, there are knowledge and practice to purify waste water to meet different purposes, such as drinking water and other non-potable uses like agriculture irrigations and groundwater protection from salt water intrusion. However, wastewater treatment and water reuse industries have faced newer challenge since as early as 1985 when it had been realized that traces of drugs could enter water cycle through pharmaceutical industries and domestic uses (Richardson and Bowron, 1985;

Halling-Sørensen *et al*, 1998; Ternes, 1998). In Sweden, Lindberg *et al* (2005, 2007) detected the presence of antibiotics in the STP and revealed that fluoroquinolones, ofloxacin, ciprofloxacin could pose potential environmental risks. Other than antibiotics, pharmaceutical compounds that passed through STP treatments with concentrations more than half of their original were diclofenac, carbamazepine, and beta blockers (Bendz, *et al* 2005). To meet the national environmental goals, Swedish government had required Swedish medical product agency to develop a report on the environmental effects of pharmaceuticals (Carlsson *et al*, 2006). The report concluded that sex hormones oestradiol and ethinyloestradiol were the ones that could pose aquatic environmental risks. However, the risk for acute environmental toxicity was deemed unlikely while chronic risks had not been able to be determined due to a lack of chronic toxicity data.

Since the early 1990s Colborn *et al* (1993) had studied that the pharmaceutical compounds that escape to the aquatic environment have been associated with the decreased fertility of birds, fish, and mammals; demasculinization and feminization of male fish, birds, and mammals; defeminization and masculinization of female fish, gastropods and birds; alteration of immune function in birds and mammals, abnormal thyroid function in birds and fish; decreased hatching success in fish, birds, and turtles.

The fact that these compounds pass through all the processes at sewage treatment plants has raised a concern. Moreover, they do not seem to degrade in the environment but negatively impact the biology of the organisms living in the recipient water body. Even though currently their presence is in minute concentrations, water reuse process requires smaller loop of water cycle and significantly faster circulations than natural hydrological cycle, which may pose danger of contaminants accumulation in a much higher rate. Although it was studied that there is no significant potential direct exposure via drinking water (Webb *et al*, 2003), there has not been any clinical study to show if this minute concentration of persistent compounds in drinking water will affect human health after a period of time. By observing the alterations they have created in the ecosystem, precautionary actions need to be taken. Moreover, the threat of PPCPs and EDCs contamination in water bodies is relevant in all parts of the world, since the world today continually progresses. PPCPs and EDCs will continue to be released in the environment worldwide, as health care and medicine accesses will keep on improving, food production will increase and create more intense agriculture, and the expansion of industries that will keep on growing especially in the developing countries.

On a more positive note, there are studies that show effective ways to remove persistent or slowly biodegradable organic compounds in wastewater treatment plants that include physical removal by membrane technology such as membrane technology such as nano-filtration and reverse osmosis, ozone treatment, advanced oxidation process and activated carbon (Ternes *et al*, 2002; Huber *et al*, 2003; Tekin *et al*, 2006; Esplugas *et al*, 2007; Snyder *et al*, 2007; Suarez *et al*, 2008). However, the drawback of these technologies is that they are costly in both investment and operations. Since PPCPs and EDCs are a growing challenge that affect all parts of the world, in which many areas cannot even afford to utilize advanced technologies, a more conventional and economical solution is more appealing and necessary to be researched on.

This study will focus on the use of chemical process to remove organic compounds, which is more economical than the advanced technologies mentioned above. The chemicals chosen are MnO_2 and KMnO_4 which have quite high redox potential but have not been commonly used in wastewater treatment plant (WWTP). MnO_2 has been much studied as a catalyst in oxidation process by ozone to remove organic compounds in aqueous solution such as oxalic acid (Andreozzi *et al*, 1996), sulfosalicylic acid and propionic acid (Tong *et al*, 2003), phenolic compounds (Martins *et al*, 2007), as well as COD and TOC (Alsheyab and Munoz, 2007). Meanwhile, KMnO_4 is commonly used in water treatment plant (WTP) to oxidize Fe and Mn, algae and other organic matter, and also to remove taste and odor in drinking water (EPA, 1999) and as a pretreatment to reverse osmosis water plant (Galvin and Mellado, 1998). KMnO_4 is also commonly used to oxidize and remove dense non-aqueous-phase liquid (DNAPL) contaminants in groundwater (Nelson *et al*, 2001). In its application in WTP, KMnO_4 can be mixed along with the coagulants in the mix tank (EPA, 1999). Due to this convenient application, the utilization of KMnO_4 (and maybe also MnO_2) may not require major alteration of a common configuration of conventional wastewater treatment plant.

Moreover, these manganese compounds possess important properties that make them potentially able to effectively remove PPCPs and EDCs and organic compounds in general. Other than its catalytic property, MnO_2 is postulated to be able to oxidize, split, and also adsorb organic compounds. KMnO_4 being a strong oxidant may oxidize and split longer chain molecules into more readily biodegradable ones while it is also being reduced to other manganese species with lower oxidation states (Mn^{6+} , Mn^{5+} , Mn^{4+} , Mn^{3+}) that can further oxidize more organic compounds.

1.2. Objectives of study

This study aims to find out the behavior and potentials of MnO_2 and KMnO_4 in removing organic compounds both by conducting literature review and laboratory experiments. The literature review mainly summarizes the recent studies done by other researchers that used MnO_2 and KMnO_4 to remove specific recalcitrant organic compounds. The experimental part focuses on the use of these manganese compounds to remove COD from typical wastewater. The use of general parameter of COD to examine the efficiency of these oxidants is appropriate to conduct time- and cost- effective research that can give valuable information regarding the effectiveness and behavior of these compounds in wastewater application. In addition, the collected information will give insights in which step of WWTP these chemicals can be suitably applied.

Overall, the COD of wastewater removed after exposure to MnO_2 and KMnO_4 will give indication to how much organic compounds are oxidized, mineralized, or adsorbed. The removal of soluble COD (SCOD) means that these organic compounds are fully mineralized and do not pose toxic effects to the environment. On the other hand, the removal of organic compounds by adsorption and flocculation that will end up in sludge may pose contamination threat to the environment through sludge disposal.

Chapter 3 of this thesis contains a summary of the behavior and ability of MnO_2 and KMnO_4 in oxidizing and removing several specific PPCP, EDC, and/or other recalcitrant organic compounds. Chapter 4 contains a series of studies/laboratory experiments that seek to find out:

- The behavior and effectiveness of MnO₂ and KMnO₄ to remove COD of two types of wastewater (sewage water influent and supernatant) performed at wastewater's natural pH (about pH 8).
- The behavior of MnO₂ and KMnO₄ reactions and how much COD gets removed when the manganese compound application is combined with flocculation process.

Based on the findings above, Chapter 5 is continued with suggestions on how to implement the utilization of MnO₂ and KMnO₄ in a wastewater treatment plant.

2. BACKGROUND INFORMATION

The section provides significant background information regarding water reuse, MnO₂ and KMnO₄, PPCP and EDC, as well as COD.

2.1. Water reuse

Water reuse is the utilization of treated wastewater to meet potable or non-potable demands that are often accompanied by the closing of the water cycle between the receiving waters for effluent and the waters for abstraction (Fig. 1). It has become an ever increasingly necessary technology that must be employed to meet challenges of increasing water demands and/or water shortages.

In general, there are four types of water reuse:

- Indirect potable water reuse
In this method, the highly treated wastewater is returned to a reservoir or other water bodies that allow dilution and mixing with the naturally existing waters for a period of time to give the opportunity for natural processes to provide additional treatment such as sunlight exposure and filtration through soil. This water is then used as raw material for drinking water treatment plant.
- Indirect non-potable water reuse
The method applied for this type of reuse is similar to indirect potable water reuse; however the level of treatment for non-potable water reuse is not as strict as the standard required for potable applications. The dilution of effluent in the watercourse is still an important factor to dilute the concentration of contaminants.
- Direct potable water reuse
In this method, the highly treated wastewater is directly introduced to water supply system without any dilution to natural water bodies or other environmental intermediate steps. However, the reclaimed wastewater may be blended with other sources of water to enter the water treatment plant to produce drinking water. Due to health concerns and negative public perception, currently it is not considered as a viable option and there is only one place in the world that practices this, which is in Windhoek, Namibia (Gentili *et al*, 2008).
- Direct non-potable water reuse
In this method, the treated wastewater is piped directly for reuse without dilution or intervention of the environment. Other than piping, it can be also injected into groundwater which can be extracted further down by the user.

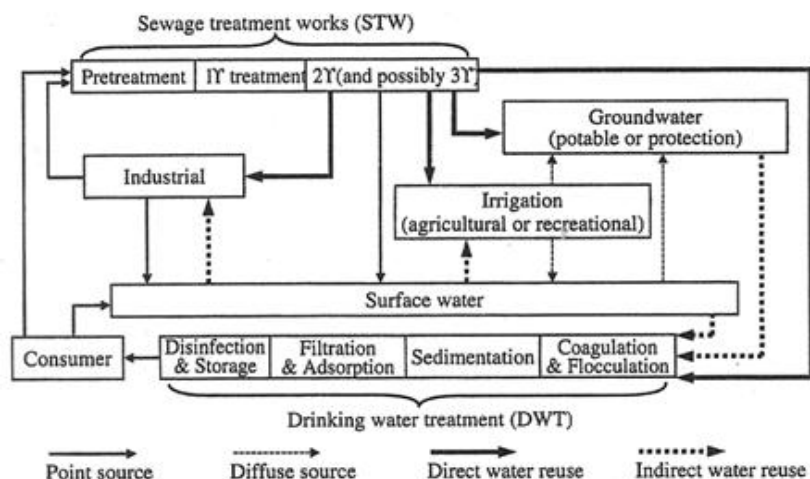


Fig. 1. The relationship between point and non-point sources, water and wastewater treatment, potable and non-potable reuse (Source: Birkett and Lester, 2003).

Due to the nature of water reuse process that actually shortens hydrological cycle, the risk of contaminant accumulation over time is also larger. PPCPs and EDCs that are currently micro pollutants in water bodies may become major contaminant in water reuse system as the water gets recycled quicker than the rate of natural water cycle. Therefore, water quality control is critical in water reuse and more technologies that efficiently remove micro pollutants such as PPCPs and EDCs should be studied and/or discovered.

2.2. Manganese compounds: MnO_2 and $KMnO_4$

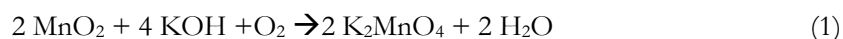
This section provides information on the origin of MnO_2 and $KMnO_4$, their speciation, redox potential and toxicity threats.

2.2.1. Sources: natural and anthropogenic

In nature, manganese occurs as minerals, not as free metal. In the earth crust, manganese concentration is about 1000 mg/kg. Manganese presence in soil depends on the geothermal characteristics of the soil, manganese speciation, activity of soil organisms and plant uptake. The weathering of manganese ore is responsible for the manganese content in water bodies, such as rivers and ocean. The precipitation of manganese in the oceans is deposited as nodules, and its concentration is about 200 mg/kg. (WHO, 1981)

One of the manganese compounds used in this study is manganese dioxide or MnO_2 . MnO_2 occurs naturally as mineral pyrolusite. Its appearance is dark black powder (solid) which is not soluble in water.

Potassium permanganate or $KMnO_4$ is a salt which is not available in nature. In fact, it is produced from MnO_2 that is fused with KOH and its reaction is as follows:



The appearance of $KMnO_4$ is purplish-bronze-gray needles and magenta-rose in solution. $KMnO_4$ is soluble in water and decomposes in alcohol and organic solvents.

2.2.2. *Manganese speciation in environment*

The source of manganese in water is coming from the surrounding soil and rocks. Manganese is present either as soluble or immobilized particulates. The mobilization of manganese occurs at low pH and low Eh. Therefore, the presence of soluble manganese is prevalent in acid mine drainage as well as in acid and poorly drained podzolic soil and groundwater. However, when soluble manganese passes through acid soil and enters streams of water that have neutral pH and Eh, the manganese got precipitated and immobilized with the sediments. In the ocean manganese is present as nodules in deep sea sediments. Human activities can also add manganese burden to the water bodies when we contaminate our soil with pesticides, fertilizers, sludge, or mine waste.

In soil, manganese can exist in different oxidation states (Mn²⁺, Mn³⁺, and Mn⁴⁺). Biological oxidation and reduction can occur in soil that transforms between the readily available Mn²⁺ and less available Mn³⁺. The oxidizing power of higher oxides increases with acidity, so the reduction by organic matter is more likely to occur at low pH values. However, if oxygen concentration is low, biological reduction can take place at any pH value. Bacterial oxidation is very slow or absent in very acid soils, therefore Mn²⁺ predominates. In alkaline soils, Mn²⁺ nearly disappears, bacterial oxidation is rapid and organic matter reduction is slow. Plants mainly absorb the readily available Mn²⁺ and the manganese availability in soil is heavily influenced by the activity of microorganisms that can alter pH and redox potentials. Reducing the soil pH or the soil aeration by flooding or compaction favors the manganese reduction to Mn²⁺, therefore increases its solubility and availability to plants. Liming and nitrogen application reduce the availability of Mn in soil. Organic material associated with high pH can produce organic complexes of Mn²⁺ leading to unavailability of this nutrient. Manganese toxicity in plants may occur in soils containing manganese levels greater than 1g/kg dry weight; this generally occurs in very acid soils and can usually be remedied by liming.

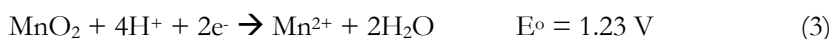
In ambient air, natural manganese level is low (0.027 µg/m³ at 823 m). However, nearly all manganese emitted into the atmosphere is in association with small particles and can be distributed over considerable distances. Common sources of particulate manganese are ferromanganese or silicomanganese industries, ambient air in manganese mines, electric steel foundry (elevated melting process), and production of steel, aluminum cans, fungicides, fertilizers and electronics, welders in industries. Medical exposure can also occur on the use of Mn as a contrast agent in medical diagnostics, ingestion by patients receiving long-term parenteral nutrition, and in drinking water (Crossgrove and Zheng 2004).

2.2.3. *MnO₂ and KMnO₄ redox potential and oxidation mechanism*

As mentioned above, manganese exists in nature in the form of minerals. The most abundant compounds as minerals are the oxides (pyrolusite, manganite, hausmannite), sulfides (manganese blende and hauerite), carbonates (manganesespar), and silicates (braunite, tephroite, knebelite, rhodamite). The speciation relative to pe-pH diagram for Mn-CO₂-H₂O system is given at Figure 2.

MnO₂

MnO₂ reduction is favored in acidic condition with half reaction as follows:



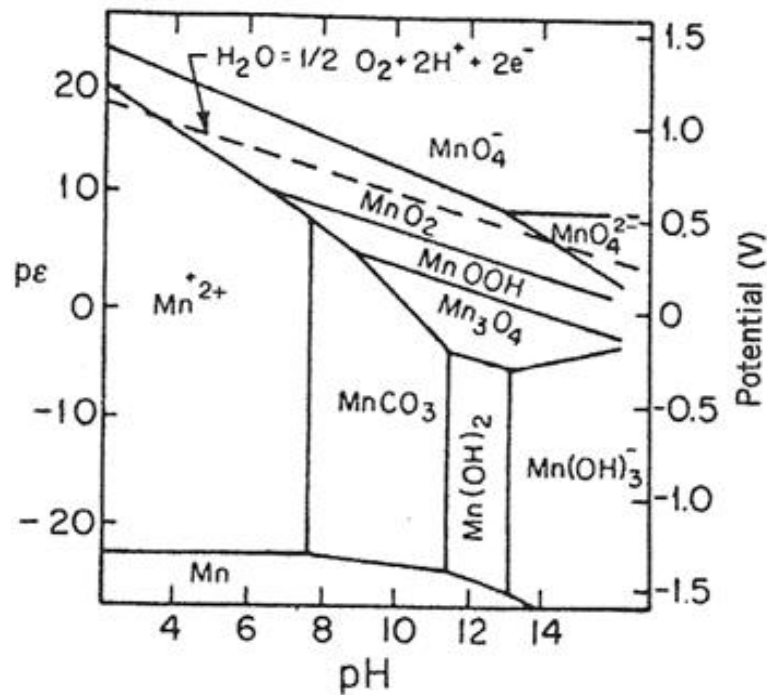


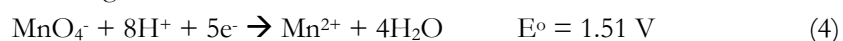
Fig. 2. *pe-pH diagram of Mn-CO₂-H₂O at 25°C (Source: Stumm and Morgan, 1996).*

Other than as pyrolusite, MnO_2 can also be formed through biological reaction. The formation of biological MnO_2 and the catalytic mechanism of organic compound oxidation as a result thereof are explained by de Rudder *et al* (2004). In a humic rich environment, bacteria can utilize biologically recalcitrant organic carbon contained in humic substances to oxidize Mn^{2+} available in nature. After being oxidized, the manganese precipitates as slime layers. As a result, the precipitated manganese can oxidize humic and fulvic acids and form lower molecular organic compounds. These compounds will then be available for further Mn^{2+} oxidation. In addition, MnO_2 is a solid oxidant that provides active sites on the oxide surface so that organic compounds and metals can be adsorbed onto them and further oxidized, or flocculated as precipitates and removed from the system. MnO_2 is also known for its catalytic effect that enhances oxidation processes by other strong oxidant compounds.

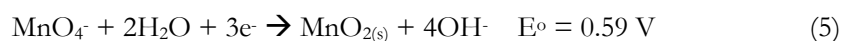
KMnO_4

MnO_4^- is a strong oxidant, where Mn has oxidation state of +7 that has high *pe* at low pH. The pH strongly influences the redox potential of KMnO_4 for it is known that KMnO_4 oxidation would produce Mn of various oxidation states (Mn^{6+} , Mn^{5+} , Mn^{4+} , Mn^{3+} , Mn^{2+}) depending on the reactant and the pH of the system. The redox potentials under different pH conditions are described below:

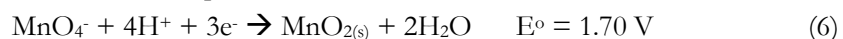
In strong acid solution:



In alkaline solution:



In acidic-neutral pH:



KMnO₄ is known to readily oxidize alkene carbon-carbon double bonds and is potential in oxidizing aromatic double bonds (Aleboyeh *et al*, 2009). It is also known to increase biodegradability of phenolic compounds. The permanganate ion can oxidize organic compounds through several pathways which include hydrogen abstraction, electron abstraction, incorporation of oxygen atom into structure, and hydride-ion abstraction. KMnO₄ can have toxic effect on microorganisms since phospholipids within cell membrane are susceptible to permanganate oxidation at carbon-carbon double bonds and can lead to cell death (Waddell and Mayer, 2003).

As organic oxidation takes place, KMnO₄ can be reduced to MnO₂ as its intermediate product. Jiang *et al* (2009) suggested a role of MnO₂ in enhancing phenolics oxidation by KMnO₄. The organic compounds and MnO₂ surface active sites on MnO₂ can react and form complexes. These newly formed complexes can be quickly oxidized by Mn⁷⁺ with a much higher rate than other organic compounds in solution. This reaction is followed by the release of the oxidized organic compounds to the solution, thus causing the regenerative property of the MnO₂ active sites.

2.2.4. *Manganese toxicity*

Crossgrove and Zheng (2004) studied on the toxicity effect of manganese (Mn). They studied that Mn toxicity is evidenced primarily in central nervous system and lung tissue (following inhalation exposure). Cardiovascular, liver, reproductive and development toxicities have also been noted although to a lesser extent. In humans, excess brain Mn produces neurotoxicity that develops into a syndrome similar to Parkinson's disease called manganism. Although the symptoms of both diseases are similar, the target brain regions are different. The symptoms of manganism may include headache and insomnia, memory loss, emotional instability, exaggerated tendon reflexes, hyper-myotonia, hand tremor, speech disturbances and festinating gait.

Mechanisms of Mn toxicity is poorly understood, however, some studies suggested that it is associated with its interaction with other essential trace elements, such as iron, zinc, copper, aluminum. High Mn concentration can increase Fe uptake and accumulation in neurons that consequently produce cellular oxidative stress that can lead to neuronal damage.

Liver damage may also occur as Mn increases the activity of the rate limiting enzyme for cholesterol biosynthesis and that bilirubin decreases the enzyme that is important in the conversion of cholesterol into bile acids. As a result, total cholesterol can get increased and bile acid production decreased.

It is also evidenced that Mn overexposure can decrease fertility and increase fetal abnormalities. Mn-exposed male workers had significantly fewer children than workers who were not exposed. In toxicological studies, the rats that received Mn injections had reduced fetal body weight. The number of litters with abnormal limb flexures and skeletal malformations also increased.

2.3. PPCP and EDC

This section provides background information on PPCP and EDC as well as an overview of the currently practiced wastewater treatment technologies for their removals.

2.3.1. *Background information*

Pharmaceuticals or drugs pose threat to water quality due to their persistence feature that may make them not readily biodegradable when they enter water bodies. This persistence is purposely developed in drugs to prevent their inactivation before they give therapeutic effect following human's consumption. The drug metabolism usually converts lipophilic chemical compounds into more readily excreted polar products that are able to leave human body. About 30% of pharmaceutical compounds are excreted in feces and 70% in urine (SWITCH, 2007). In addition to their persistence nature, during drug metabolisms, some reactions can occur that form highly polar conjugates that are more toxic than the parent compound that could further harm the environment.

Personal care products is a term used to refer to common household items such as fragrances, hair and skin care products, sun-screen agents, cosmetics, insect repellents and antiseptics. Like pharmaceuticals, these items contain chemicals that are also persistent in the environment and not removed by WWTP processes. In water quality, pharmaceuticals and personal care products are group together as emerging contaminants which entry to the WWTP and environment is mainly through domestic households, industries, hospitals, animal farming, agriculture, and aquaculture (Ellis, 2006).

Endocrine disruptor compounds are organic compounds that act like hormones in the endocrine system and disrupt the physiologic function of endogenous hormones. The list of EDCs includes pesticides, persistent organohalogenes, alkyl phenols, heavy metals, phytoestrogens, and synthetic and natural hormones (Birkett and Lester, 2003). Some PPCPs cause harmful effect to the endocrine system that they are being classified as EDCs as well.

The negative impacts of PPCP may include negative hormonal and toxic effects in numerous organisms, phytotoxicity toward certain plants (Xia *et al*, 2005), and causing bacteria resistance to antibiotics. The effects of EDCs in human beings may include the reduction of human sperm, increase incidence of breast, testicle, and prostate cancers, and the endometriosis (Esplugas *et al*, 2007).

PPCPs and EDCs have been detected in treated wastewater effluents at concentrations ranging from 1.0 ng/L to 1.0 µg/L due to incomplete removal during treatment processes (Esplugas *et al*, 2007). The discharge of WWTP effluent makes an entry point for the presence of these compounds in the surface water system, while the reuse of treated wastewater in agricultural application may introduce these compounds to the soil. Since these compounds are usually highly polar, they can be leached down in soil and contaminate the groundwater.

2.3.2. *PPCP and EDC removals in WWTP*

Carballa *et al* (2004) investigated the fate of 10 PPCP and 3 EDC compounds in conventional sewage treatment plant. The results indicated that the chemicals removed during primary treatment were lipophilic compounds such as fragrances that got removed with fat separation and adsorbed onto solid surfaces. Secondary treatment or activated sludge was able to partially remove the investigated compounds, except for contrast agent iopromide. Overall, the removal efficiencies of WWTP were about 70-90% for the fragrances, 40-65% for anti-inflammatories, and 60% for antibiotic. This study shows that each compound has specific characteristics and therefore required diverse method of removals. Other study (Balest *et al*, 2008) also confirmed that EDC compounds such as

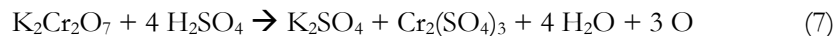
estrone, 17 β -estradiol, bisphenol A, 4-tert-octylphenol could be partially removed by conventional activated sludge, but an enhanced biological reactor called Sequencing Batch Biofilter Granular Reactor (SBBGR) was more effective in removing such compounds.

A review by Suarez *et al* (2008) regarding the removal of PPCPs and EDCs concluded that conventional WWTP treatment processes cannot remove compounds that are highly persistent and cannot be sorbed or biologically transformed. To encounter this problem, they suggested that physico-chemical of PPCP in both liquid and solid phase should be studied to predict the removal mechanism. Suarez *et al* (2009) reported that coagulation and flocculation by FeCl₃ and Al₂SO₄ effectively removed musk fragrances from hospital wastewater, again, due to the lipophilic character of fragrances that promoted interaction with lipid fractions of solids. However, anti-inflammatories like diclofenac, naproxen, and ibuprofen were not removed efficiently (20-40%). Meanwhile, anti-epileptic drug carbamazepine, anxiety reliever diazepam, contrast medium iopromide were not removed at all. Other than coagulation flocculation, oxidation has also been studied to remove persistent compounds. Jiang *et al* (2005) investigated the removal of EDC compounds, such as BPA, estrone, and 17 β -estradiol by Ferrate (VI) and electrochemical oxidation. These methods can reduce the studied EDC compounds to very low levels (10-100 ng/L). Oxidation by ozonation also increased the biodegradability of carbamazepine in sewage sludge prior to anaerobic digestion process (Carballa *et al*, 2007). Other advanced technologies that could efficiently remove some PPCP and EDC compounds were already mentioned on section 1.1.

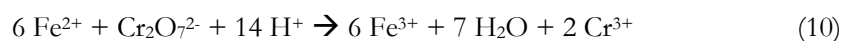
2.4. The use of COD as a parameter of organic compounds removal efficiency

In general, Chemical Oxygen Demand or COD in water quality is considered as the representation of pollution level in domestic and industrial wastewater or of contamination level in water bodies. The level of pollution/contamination is determined in terms of total oxygen required to oxidize the organic materials to CO₂ and water. COD value is determined from the oxidation of organic matter (biodegradable and non-biodegradable) by strong oxidizing. Commonly, COD is used to define the strength of wastewater containing non-biodegradable organic substances that inhibit biological activity.

COD analysis is normally done by converting the organic matter to carbon dioxide and water by heating with potassium dichromate (K₂Cr₂O₇) in an acidic media containing silver sulphate. Their chemical reactions are as follows:



The excess of dichromate that is not oxidized is titrated with ferrous ammonium sulfate (FAS) using ferroin indicator. The dichromate reduces to Cr³⁺ which produces green color to the reaction solution. At the end point, the green color discharges and reddish-brown color of the indicator remains. The reduction of the excess dichromate is describes as follows:



Therefore, COD analysis by this method implies that the amount of oxidizable organic matter is proportional to the K₂Cr₂O₇ consumed.

In most studies regarding pharmaceutical wastewaters, other than specific compound removals, the removal of COD was also investigated. Generally, COD can be effectively removed by biological treatment. Biological process such as SBR (Sequencing Batch Reactor) and advanced SBBGR (Sequencing Batch Biofilter Granular Reactor) can remove more than 90% COD (Stamatelatou *et al*, 2003; Balest *et al*, 2008). However, in pharmaceutical industry applications, pharmaceutical wastewater normally contain high COD water and low BOD, indicating low biodegradability characteristic and therefore, difficult to remove by biological process. Oxidation processes such as ozonation (Balcioglu and Ötker, 2003), Fenton's reagent (San Sebastian Martinez *et al*, 2003), and combination of Fenton-like oxidation with Fe(III) precipitation and lime coagulation (Kulik *et al*, 2008) were proven to be able to partially remove COD and increase the biodegradability from wastewater of pharmaceutical industries and helped to meet the requirement for sewage discharge. Due to the combination of oxidation and physical-chemical nature of COD removal, COD measurement is divided into fractions of total COD that are associated to particulates and soluble. Oxidation may effectively increase solubilization of COD and affect the concentration of soluble COD, while coagulation and flocculation may adsorb COD in the particulates and affect the concentration of particulate COD.

An especially relevant study to this thesis was conducted by Jiang *et al* (2005) that investigated the use of oxidation by Ferrate(VI) and electrochemical processes which effectively removed EDC compounds: BPA, estrone, and 17 β -estradiol. In addition, Ferrate(VI) as a high oxidation agent could remove more TCOD and SCOD than electrochemical process did. It indicated that Ferrate(VI) has a high potential in removing EDC compounds and other organic contaminants present in wastewater.

3. REVIEW OF THE MnO₂ AND KMnO₄ USE FOR PPCPs AND EDCs REMOVAL

There has not been much research done to explore the potential of MnO₂ and KMnO₄ to remove organic compounds for wastewater application. This chapter provides an overview from the few recent researches that used MnO₂ and KMnO₄ to remove specific PPCPs and/or EDCs.

3.1. MnO₂ applications to remove PPCPs and EDCs

Current studies have indicated that MnO₂ is potential to effectively remove PPCPs and EDCs. The effectiveness of MnO₂ oxidation is affected by initial MnO₂ concentration, pH, and the presence of co-solutes (Lin *et al*, 2009) and NH₄⁺ (Forrez *et al*, 2009).

Lin *et al* studied that Bisphenol A or BPA (a compound used in the production of plastics) removal efficiency was increased at higher initial MnO₂ concentrations due to the increase in the availability of accessible sites on the oxide that created the increasing ratio of the oxide surface area to BPA moles in the solution. This suggests that in low MnO₂ concentrations, a saturation of occupied oxide sites by BPA was possible which would reduce the reaction rate and removal efficiency.

In addition, BPA removal efficiency varies under different pH values; it is most effective (100% removal within 10 mins) in acidic condition (pH 4.5 and 5.5), moderately effective (90-100% within 60 minutes) in basic condition (pH 8.6 and 9.6), and least effective (40-60% within 60 mins) in neutral condition (pH 7.5 and 6.5). It is known that MnO₂ oxidation

potential occurs in acidic solution (see Eq. 1) since the reduction of MnO_2 requires the participation of H^+ for the reaction to occur. Therefore, it is expected that BPA removal would be more efficient under acidic condition. However, the BPA removal efficiency is also affected by the speciation of BPA in a solution that is depended on pH, since pH affects the electron transfer process between BPA and MnO_2 . A protonated organic compound is less reactive to the oxidation process compared to the deprotonated ones. Under neutral pH, almost all BPA remain undissociated thus they are less susceptible to MnO_2 oxidation, rendering very inefficient removal.

Lin *et al* also found out that the presence of coexisting metal ions, Ca^{2+} , Mg^{2+} , Fe^{3+} , Mn^{2+} inhibit the BPA removal. Metal ions tend to complex with the dissolved and sorbed reactants and also compete to occupy the surface sites of the oxides. In addition, higher metal ions concentrations cause the increased occupation of reactive sites on MnO_2 . The strongest inhibitor is Mn^{2+} followed by Ca^{2+} , Mg^{2+} and Fe^{3+} . Therefore, since Mn^{2+} is also a product of MnO_2 , an increase in Mn^{2+} reduces the redox potential of MnO_2 and results in progressively slower reaction rate. Forrez *et al* also noted that the presence of NH_4^+ inhibits oxidation process due to its adsorption to the negatively charged MnO_2 surface, blocking the active sites for the organic compounds to oxidize.

Other than in aqueous solution, organic compound oxidation by MnO_2 was also studied in a bioreactor bed. De Rudder *et al* (2004) and Forrez *et al* (2009) studied the removal of 17α -ethynylestradiol (EE2) by passing the chemical through MnO_2 bioreactor. EE2 is a compound present in contraceptives, persistent in the environment, and able to be converted into its active form even though it is excreted from the body as conjugates. EE2 removal occurred due to MnO_2 oxidation and adsorption capabilities and the biodegradation by biomass. De Rudder *et al.* observed the removal efficiency of EE2 was 82%. They also observed the presence of biomass in the middle of the reactor column where most of the adsorption occurred. They also found out that the capacity of the MnO_2 bed exceeded the theoretical adsorption capacity. The calculated theoretical adsorption capacity was 6 days but EE2 was still removed from the water sample even after 40 days of monitoring. These conditions suggests that EE2 was adsorbed to the MnO_2 granules and also degraded by the biomass into compounds with little or no estrogenic activity, rendering a self-regenerating property of MnO_2 . This makes MnO_2 bed reactor a cost effective treatment since the matrix does not have to be replaced. Forrez *et al* further showed that mineral MnO_2 has regenerative capacity in removing EE2, while biologically formed MnO_2 (by bacteria that oxidize Mn^{2+} to MnO_2) does not. Additionally, they also found out that ammonia-oxidizing bacteria were important in the degradation of EE2 and suggested that a post-treatment nitrifying reactor supplemented with ammonium offers a solution for biological removal of EE2.

3.2. KMnO_4 applications to remove PPCPs and EDCs

KMnO_4 was studied by Jiang *et al* (2009) to examine its efficiency in removing triclosan. Triclosan is a compound widely used in personal care products such as soap, deodorant, toothpaste and cosmetics. It is commonly found in surface water in trace amount, however it is toxic and when exposed to sunlight, triclosan could transform into highly toxic polychlorinated dioxin. Triclosan has electron rich phenolic property that can be oxidized by Mn^{7+} .

The study by Jiang *et al* showed that KMnO_4 application at pH 5 was more effective in removing triclosan than its application at pH 7 as it was accompanied by autocatalysis reaction through MnO_2 formation that resulted in a more rapid triclosan removal. The removal of triclosan in natural and waste waters reached to 70-80%.

Similar to the dye removal, phenolic compound oxidation by KMnO_4 is also pH dependent. The adsorption of phenols onto oxide active sites decreases at higher pH due to deprotonation of the substrate or the more negative MnO_2 surface charge.

Jiang *et al* also found out that the presence of phosphate and other ligands, such as EDTA, pyrophosphate and humic acids increase the KMnO_4 oxidation of phenolic compounds. It is suggested that the presence of ligand creates an effect with the formed soluble manganese intermediate molecules (Mn^{6+} , Mn^{5+} , and Mn^{3+} species) as KMnO_4 oxidizes phenols. In the absence of ligands, these manganese intermediate species would self decompose and disproportionate spontaneously rather than participate in the oxidation of phenolics. In the presence of ligands, the manganese intermediate molecules may be stabilized by the ligand and therefore can be effectively utilized as oxidant.

KMnO_4 has also been used for a study to remove dye wastewater (Aleboeyh *et al*, 2009; Liu *et al*, 2010). Although dye is not categorized as PPCP or EDC, its wastewater has harmful characteristics, such as difficult to treat, has high COD and color intensity, and also is toxic and carcinogenic. Both studies showed that effective decolorization of dye wastewater is achieved by KMnO_4 application under pH 2, since the redox potential of KMnO_4 increases with the decrease of pH. Low pH also resulted in highest Dissolved Organic Carbon (DOC) removal, except when pH is between 1 and 2.8 indicating that at this range the degradation product of the dye was inhibitive to the removal of DOC.

TOC removal was also studied to indicate the mineralization of the dye. When excess KMnO_4 concentrations were applied, it resulted in higher TOC removal (up to 40%) over 7 hours of contact reactions. However, after 24 hour of treatment period, complete mineralization could not be achieved.

Other than its strong oxidation potential property, KMnO_4 is appealing because the reduced form as MnO_2 can further degrade the organic compounds due to its oxidation, catalytic, and adsorption potentials (see Ch 2). Liu *et al* (2010) did research on the effectiveness of KMnO_4 oxidation alone, MnO_2 adsorption alone, and the combination of KMnO_4 oxidation and MnO_2 adsorption. The study revealed that oxidation potential of KMnO_4 is stronger than MnO_2 as seen from the lower intensity of the dye absorption by UV-vis spectrometry indicating more complete discoloration. On the other hand, MnO_2 was able to significantly remove DOC (52%) in less time due to its good adsorptive property. However, the longer reaction time decreased DOC removal as the oxidation of dye and the resulting oxidized dye compound could detach the dye compound from the active sites. The KMnO_4 oxidation and MnO_2 adsorption did remove DOC (39%), but the oxidized dye compounds were more difficult to adsorb onto the MnO_2 surface rendering less efficiency in DOC removal. The KMnO_4 oxidation alone contributed to the least DOC removal (27%) indicating that the dye is very recalcitrant (contain benzene ring, $-\text{C}_2\text{H}_5$, organic acids) that KMnO_4 oxidation at pH 0.5 could hardly degrade them.

To study the mechanisms of the three processes, the Mn²⁺ concentration in the samples were monitored. Oxidation of dye compounds by KMnO₄ at pH 0.5 resulted in complete Mn⁷⁺ reduction to Mn²⁺ as there were no particles present in the solution and the solution was kept clear. MnO₂ adsorption process resulted in increase of Mn²⁺ concentration as time progressed, indicating that the adsorption of the dye compound into MnO₂ surface actually led to the oxidation of the substrate that reduced the Mn⁴⁺ to Mn²⁺. As for the combined KMnO₄ oxidation and MnO₂ adsorption, the dissolved Mn⁷⁺ decreased steadily over time. At the final reaction time, the dissolved Mn concentrations were much lower than the dissolved they were in MnO₂ adsorption process. It indicated that most Mn⁷⁺ were transformed into solid MnO₂ instead and not further reduced to Mn²⁺, which suggested that there was not much oxidation taking place between oxidized dye compounds and MnO₂.

The highest biodegradability of dye compounds was achieved by KMnO₄ oxidation at pH 0.5 which gave off the highest BOD₅ value and BOD₅/DOC ratio. This fact made KMnO₄ a feasible solution as pre-treatment before biological process. On the other end, the lowest biodegradability was found in MnO₂ adsorption, although the process actually gave off the highest DOC removal.

4. LABORATORY EXPERIMENTS

The laboratory experiments were conducted to give additional information regarding the efficiency and behavior of MnO₂ and KMnO₄ in removing COD from wastewater at the wastewater's natural pH. Two types of wastewater were used: inlet water of Henriksdal WWTP and supernatant from Bromma WWTP. This experiment was conducted to focus on the effect of MnO₂ and KMnO₄ to remove COD in influent sewage water of Henriksdal Reningsverk (WWTP). Both total and soluble COD were examined to find out the oxidation effect in both compartments. In addition, combination of manganese compound treatment and magnesium-calcium precipitation was investigated. Precipitation by magnesium compounds at high pH is known to be able to efficiently remove COD, suspended solids, organics, turbidity, phosphate, and also ammonium (Semerjian and Ayoub, 2001; Mi, 2009). The effect of MnO₂ and KMnO₄ to remove COD in supernatant from Bromma WWTP was also investigated. Supernatant usually contains higher COD concentration and lower suspended solids. Both unfiltered and filtered supernatant water samples were used.

4.1. Materials and method

4.1.1. COD removal from Henriksdal WWTP inlet water

The water used for the study was the influent sewage water of Henriksdal wastewater treatment plant that was also accessible for collection at Hammarby Sjöstadverket pilot plant. Sewage water was collected every morning and used for the experiments conducted on the very same day. The average concentration of total suspended solid (TSS) is 283 mg/L. The COD concentration of this water varied from day to day and throughout the experiment period. The collected sewage water had TCOD concentrations ranging from 309 mg/L to 565 mg/L and SCOD of 136 mg/L to 234 mg/L.

A MnO₂ concentration of 2750 mg/L was used in this experiment regardless of the COD concentration of the sewage water. This amount was calculated based on stoichiometric of MnO₂ reduction to Mn²⁺ that

could oxidize sewage water with COD concentration of 500 mg/L. Due to its insolubility in water, MnO_2 powder was directly weighed and applied as solids to the reaction flasks. In contrast, KMnO_4 was prepared as liquid solution. KMnO_4 is soluble in water and produces an intense pink/purple color. A solution of 2500 mg/L KMnO_4 was prepared daily to be used for the experiments conducted for the day. KMnO_4 readily degrades and undergoes photolysis when exposed to the sun. Therefore, the KMnO_4 solution could not be kept for more than one working day. According to stoichiometric calculation of KMnO_4 reduction to Mn^{2+} , to oxidize sewage water with 500 mg/L COD, 1975 mg/L of KMnO_4 was needed. In reality, based on preliminary experiments conducted beforehand, when the correct amount was applied, KMnO_4 did not get fully reduced even after two weeks of reaction period. Moreover, the intense purple color interfered with the spectrophotometer reading on COD analysis resulting in unreliable measurements. Therefore, an experimental or trial and error approach was done to determine the dosage application to make sure that the KMnO_4 was fully reduced (purple color disappeared) at the end of reaction period. Based on this trial and error, KMnO_4 concentrations of 30 mg/L were applied for the 4-hour treatment and 120 mg/L for the 24-hour treatment.

Magnesium calcium coagulation was prepared by using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and CaCl_2 . The concentration of Mg^{2+} was chosen to be 15 mg/L based on previous study that showed an effective phosphates removal (Mi, 2009). $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio was chosen to be 1, so concentration of Ca^{2+} was also 15 mg/L. The pH of the solution in reactor was adjusted to a value of 10.5 – 10.7 by 10% NaOH in order to provide an alkaline environment required for effective precipitation to take place (Mi, 2009).

Total and soluble COD analyses were done by using Hach-Lange® COD cuvette test. For TCOD measurement, water samples were extracted directly from the reactor without any filtration, while SCOD analyses were done for water samples taken from the filtrate of 0.45 μm membrane filtration.

Discontinuous bench-scale experiments were conducted to test the efficiency of MnO_2 and KMnO_4 in removing total and soluble COD. For each MnO_2 and KMnO_4 treatment, a series of 4 experiments were done. These experiments were:

- Sewage water receiving treatment for 4 hours
- Sewage water receiving treatment for 24 hours
- Sewage water receiving treatment for 4 hours, followed by high-pH magnesium and calcium precipitation
- Sewage water receiving treatment in concurrent with high-pH magnesium and calcium precipitation

Simple bench-scale reactor was utilized; a 500 ml flask was used to contain 400 ml of sewage water and the determined dosage of chemical treatments. Throughout the experimental period, the water was continuously stirred by magnetic stirrers at a speed of 300 rpm. The flasks were covered by parafilm to make sure that no oxidation might occur due to the oxygen influence from the ambient air. At the end time of each treatment, COD analyses were conducted immediately afterwards (on the same day). The pH of the water was not adjusted in this study. The oxidation processes occurred under normal-alkaline pH of the waste water that ranged between 7.8 and 8.2. The electrical conductivity of the water was relatively stable from day to day and the values ranged about 1-2 mS/cm. Each experiment was conducted in two replicates.

For high-pH magnesium and calcium precipitation, the determined dosages of Mg²⁺ and Ca²⁺ were added to 400 ml sewage water that was under continuous stirring at 400 rpm, followed by pH adjustment that was also immediately made until pH reached 10.5 – 10.7. This rapid mixing was done for 10 minutes before the speed was lowered to 50 rpm for 30 minutes to allow flocculation to occur. The flask was then removed from the stirrer to sit undisturbed to let the flocs settle on the bottom of the flask. After 30 minutes of settling, COD analyses were performed.

COD analyses were done by Hach Lange® cuvette tests. The water sample was reacted with sulphuric acid – potassium dichromate solution with the presence of silver sulphate as catalyst. Chloride was masked by mercury sulphate and then the green coloration of Cr³⁺ was measured by Hach Lange® Ion 500 spectrophotometer.

4.1.2. *COD removal from Bromma WWTP supernatant*

Water from sludge dewatering process was obtained from Bromma WWTP in February 2010, which had average TSS value of 148 mg/L and average TCOD and SCOD values of 630 mg/L and 383 mg/L, respectively. Similar to the experiment described in section 4.1, the supernatant water was treated with 2750 mg/L MnO₂ and 60 mg/L KMnO₄. The solutions were stirred for 4 hours before TCOD and SCOD analyses were done. In addition, to find out the efficiency of the chemical in removing SCOD alone, another set of water samples was prepared. The supernatant water was filtered through 0.45 µm membrane filter and MnO₂ and KMnO₄ were applied to the sample and stirred for 4 hours. This filtered water had original SCOD of 536 mg/L. The pH of unfiltered supernatant was 8 and 7.5 for filtered supernatant.

4.2. Result

4.2.1. *COD removal from Henriksdal WWTP inlet water*

MnO₂

The 24-hour MnO₂ treatment resulted in the highest total and soluble COD removals of 61.3% and 46.2%, respectively, which was higher than 4-hour treatment that had TCOD and SCOD removals of 42.8% and 26.8% (Fig. 3). Adding Mg-Ca flocculation process after the sewage water being treated with MnO₂ for 4 hours did not enhance the removal of COD (totally, 44.9% TCOD removed and 28.2% SCOD removed). Both total and soluble COD removals were about as the same as achieved by 4-hour MnO₂ treatment alone. In addition, concurrent oxidation by MnO₂ and flocculation treatment apparently resulted in the lowest TCOD and SCOD removals (39.4% and 2.9% respectively).

KMnO₄

Three unexpected result were observed in the experiment using KMnO₄. First of all, the 24-hour treatment did not remove more TCOD than 4-hour treatment did (Fig. 4). Second, the SCOD removal by KMnO₄ was quite low. The highest SCOD removal was achieved by the concurrent treatment (13.3%). Meanwhile, KMnO₄ treatment for 4 hours only resulted in 2.8% removal and negative SCOD removals were observed in the 24-hour treatment (-2.4%) as well as in the 4-hour treatment followed by flocculation (-2.4%). The third unexpected result is that the concurrent treatment of oxidation and flocculation gave a high TCOD removal (58.9%) and very clear water (high transparency) after a very short period of contact time.

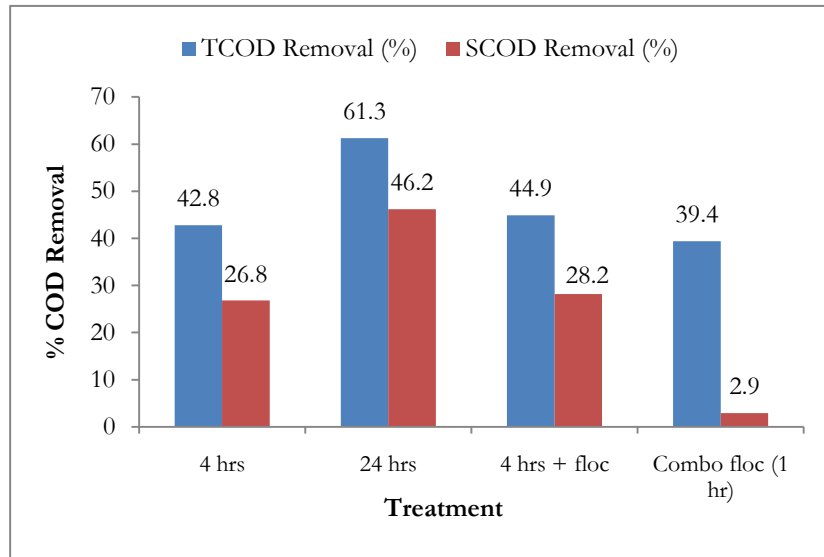


Fig. 3. COD removal from Henriksdal influent by MnO_2 .

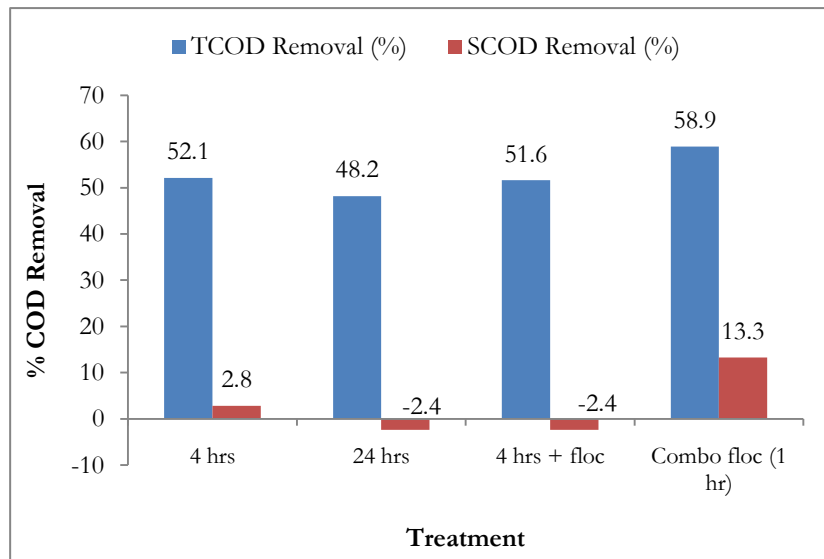


Fig. 4. COD removal from Henriksdal influent by $KMnO_4$.

4.2.2. COD removal from Bromma WWTP supernatant

After 4 hours of MnO_2 exposure, TCOD and SCOD of the supernatant removed were 21.1% and 7.3% (Fig. 5), while $KMnO_4$ treatment removed 39.2% of TCOD and 11.8% of SCOD (Figure 6). In the filtered sample, $KMnO_4$ was able to remove 9.9% of SCOD (designated as FSCOD in the graph) and MnO_2 was only able to remove 3.7%.

4.3. Discussion

4.3.1. General discussions

The MnO_2 application in Henriksdal influent at pH 8 resulted in significant total and soluble COD removals, especially when given a longer time of reaction. The higher TCOD and SCOD removals by 24-hour treatment compared to 4-hour one indicated that even after 24 hours there were enough available active sites on the surface of MnO_2 to both oxidize and adsorb COD. Given the high concentration of initial MnO_2 ,

it was not likely that the active sites were the limiting process of the reaction in this study; instead it might have been the pH of the influent wastewater. A more effective removal might be possible to achieve by lowering the pH. Equation 3 (refer to Ch 2) shows that acidic environment is needed for MnO_2 reduction to Mn^{2+} . In fact, when pH is decreased from 8 to 4, MnO_2 redox potential is increased from 0.76 to 0.99 (Lin *et al.*, 2009; Stumm and Morgan, 1996). However, this experiment showed that in neutral-alkaline pH, MnO_2 was able to remove quite significant TCOD and SCOD from the wastewater, given a long period of reaction time; and that majority of the COD removed were in the soluble compartment.

The magnesium-calcium precipitation following 4-hour MnO_2 treatment did not remove more particulate COD than soluble COD (i.e. SCOD was still the majority fraction of COD removed). The inefficiency of magnesium-calcium precipitation in the presence of MnO_2 could be caused by the inhibition effects by the ions introduced for flocculation (Mg^{2+} and Ca^{2+}). Therefore, it was possible that after 4 hour oxidation, and when Mg^{2+} and Ca^{2+} were introduced, the added salt ions would quickly occupy the available sites instead of forming magnesium-calcium precipitates. As in the case with concurrent oxidation and flocculation treatments, when MnO_2 , Mg^{2+} and Ca^{2+} were introduced into the reactor at the same time, the salt ions might have quickly inhabited the active sites of MnO_2 , resulting in no magnesium-calcium precipitation. In this particular experiment, considering the high concentration of MnO_2 , the low value of COD removal was unlikely due to the competition of active sites between the organic compounds and salt ions. In fact, the majority of COD removed was adsorbed as particulates and the low removal rate of SCOD might be due to the short contact time (less than 1 hr) between organic compounds and MnO_2 active sites.

The results regarding KMnO_4 application in Henriksdal influent are a bit more challenging to interpret. The removal of TCOD in 24-hr treatment was lower than the one in 4-hr treatment. This result was unexpected as longer period of time should have allowed more oxidation to take place. Moreover, as KMnO_4 is reduced to MnO_2 and other intermediates, more COD should have gotten removed as the intermediate compounds are also able to oxidize and adsorb organic compounds.

Another odd finding was the very low and even negative SCOD removals in three out of four treatments involving KMnO_4 . It raised questions if there were some organic compounds that got solubilized within the flask during KMnO_4 treatment or if it was a mere analytical error. Based on the repeated pattern (i.e. negative COD removal) since preliminary experiment was conducted, the former was believed to be true. The increased concentration of soluble COD in the flask might be caused by high efficiency of KMnO_4 in breaking down carbon-carbon double bond of organic compounds that degraded and transferred particulate COD into soluble pool. A further explanation of this behavior is written in section Appendix III.

The third unexpected results regarding highly clear water resulting from concurrent KMnO_4 treatment with Mg-Ca precipitation is elaborated in more detail in section 4.3.2.

Since there is a high degree of uncertainty in the SCOD values in KMnO_4 treatments, the values of both TCOD and SCOD obtained are not reliable and this set of experiment cannot justly indicate the effectiveness of KMnO_4 in removing COD from sewage water. And since

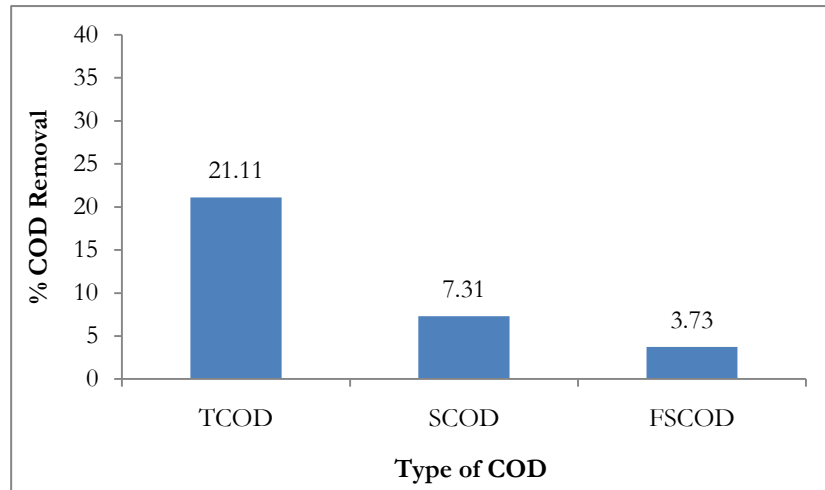


Fig. 5. COD removal from Bromma supernatant by MnO_2 .

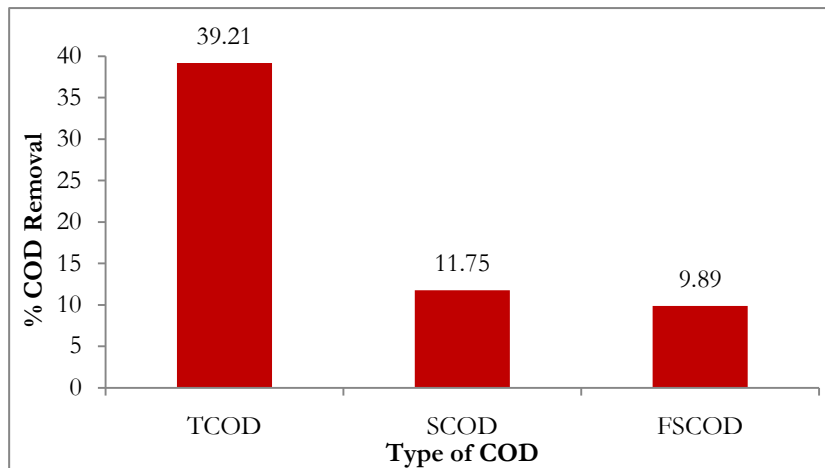


Fig. 6. COD removal from Bromma supernatant by $KMnO_4$.

$KMnO_4$ has tendency to break down and solubilize particulate organics, a follow up experiment using filtered and unfiltered supernatant from Bromma WWTP was conducted to test its efficiency in removing COD of water that had lower concentration of total suspended solid.

The results of the experiment showed that $KMnO_4$ was able to oxidize more soluble organic compounds than MnO_2 , which was expected because of higher oxidation state of Mn in $KMnO_4$. This was not clear in the experiment with Henriksdal wastewater, since $KMnO_4$ true ability to remove SCOD was masked by its effectiveness in solubilizing suspended organics.

4.3.2. *Concurrent $KMnO_4$ oxidation and Mg-Ca flocculation*

In $KMnO_4$ treatment of Henriksdal sewage water, the highest TCOD removal was achieved by concurrent treatment of oxidation and flocculation with 58.9% removal (Fig. 4). In this treatment, $KMnO_4$ was applied into continuously stirred sewage water, and consecutively followed by Mg^{2+} and Ca^{2+} application and then NaOH for pH adjustment. The total amount of time for these chemical additions was around 10 minutes. This concurrent treatment was interesting because from physical/visual observation, the flocs that formed during the process were white flocs, which were expected from magnesium-calcium precipitation. In fact, as

the compounds were added to the flask, KMnO_4 discolored very quickly/within minutes (Fig. 7) although the applied dosage was half of the dose applied to the 4-hour treatment (15 mg/L) with a consideration that this reaction would take place only in less than 1 hour.

A possible explanation for this rapid discoloration is that as Mg^{2+} and Ca^{2+} were applied to the waste water; the hydrogen ions (H^+) were also released making the solution a little bit more acidic. The higher H^+ activity favored the KMnO_4 reduction as it was reduced to MnO_2 . This created an autocatalytic effect that caused the MnO_2 -bound organic compounds to undergo a more rapid reaction rate as it was oxidized by Mn^{7+} . At the same time the Mg and Ca ions were able to trap, flocculate the colloids and suspended solids, and provide good settling.

As a result, this process could remove significant amount of COD in a short period of time with lower initial KMnO_4 concentration. This combination treatment also was able to give off much clearer water/better transparency than normal KMnO_4 treatment (Fig. 8). In addition, the 4-hour KMnO_4 treatment followed by Mg-Ca precipitation also gave clear water (Fig. 9). However, it was not investigated further if it was able to remove more COD than KMnO_4 treatment alone. In any case, it indicated that the Mg-Ca flocculation was able to trap the colloids that give color to water and settle them, thus enhancing the clarity of treated sewage water.

Overall, the results of this process (i.e. high water clarity, good settling of solids, and the potential of enhancing organics biodegradability caused by KMnO_4 oxidation) make this combination chemical process appealing to be applied for chemical treatment in wastewater treatment plants. Moreover, the fact that KMnO_4 -flocculation combination treatment is also commonly used in water treatment plant supports the notion that its application in the wastewater treatment plant is highly possible.

4.3.3. *Limitations of the study*

The laboratory study performed included some uncertainties and limitations. First of all, the wastewater samples used in the experiments were collected at different times and with different original COD concentrations (Appendix II) but they are treated with the same concentration of oxidants. Therefore, on several occasions, back-to-back comparison between some treatments could not really be done since it was unknown if the different concentrations of original COD would affect the oxidation



Fig. 7. The process of concurrent treatment of KMnO_4 and Mg-Ca flocculation



Fig. 8. Left: $KMnO_4$ treatment for 4 hours. Right: Concurrent treatment of $KMnO_4$ and Mg-Ca flocculation.

rates. Moreover, the amount of suspended solids and biomass would vary as well; their presence might have significantly impacted the removal or addition of COD. Another limitation of the study was that it was not continuous, i.e. the samples taken from 4-hr and 24-hr treatments came from different flasks, so the data presented in this thesis should not be interpreted as continuous change over time.

The result shows that indeed MnO_2 and $KMnO_4$ could remove COD from wastewater; however the experiments were not conducted based on an optimum environment. Instead they were done in the wastewater's natural condition. Therefore, the removals achieved were not necessarily the optimum efficiency. A better efficiency may be possible to achieve by conducting optimization studies to determine optimum parameters such as pH, wastewater and Mn-compounds concentrations, TSS, presence of other ions. To further find out the effectiveness of MnO_2 and $KMnO_4$ in removing recalcitrant compound such as PPCPs and EDCs, the biodegradability of the organic compounds or BOD measurement after treatments would also be necessary to investigate. In addition, the use of pharmaceutical wastewater that contain high COD and low BOD may



Fig 9. $KMnO_4$ treatment for 4 hours followed by Mg-Ca flocculation.

be more appropriate to determine the effectiveness of MnO_2 and $KMnO_4$ to enhance biodegradability. Despite of these limitations, this study is a first step to uncover the potential of MnO_2 and $KMnO_4$ as chemical treatment to remove COD in wastewater treatment application which also has opened doors for more elaborate follow up researches.

5. APPLICATION BASED ON THE FINDINGS

While the literature studies show that MnO_2 and $KMnO_4$ can degrade several recalcitrant organic compounds, the experimental results also show that they can remove COD. These findings indicate that their usage in WWTP in conventional wastewater treatment system to help remove recalcitrant organic compound is highly potential and worthy to be explored further. For an application in WWTP and using Henriksdal WWTP configuration as a model (Fig. 10), there are several locations in which MnO_2 or $KMnO_4$ can be applied:

- At or after the chemical treatment prior to biological process.
- After activated sludge to oxidize and remove the persistent organic compounds that are not removed by biological process.
- At one of the final steps just before the effluent is discharged to Baltic Sea.

According to literature studies, MnO_2 application did not efficiently enhance biodegradability of recalcitrant organic compounds. Therefore, MnO_2 application will not be that significant if put prior to biological process. Instead, its potential to remove recalcitrant organic compound is probably biggest if combined in slow sand filtration as post-treatment since contact with oxide sites is necessary for catalysis, oxidation and adsorption to take place. Plus, MnO_2 has self-regenerative property that makes it more appealing and cost effective.

The concurrent $KMnO_4$ oxidation and Mg-Ca precipitation in section 4.3.2 may be applied at the chemical treatment prior to biological process. This treatment may not specifically or directly target the removal of COD or slowly- and non- biodegradable compounds; however it may give superior performance of pretreatment that can help improve the overall water quality.

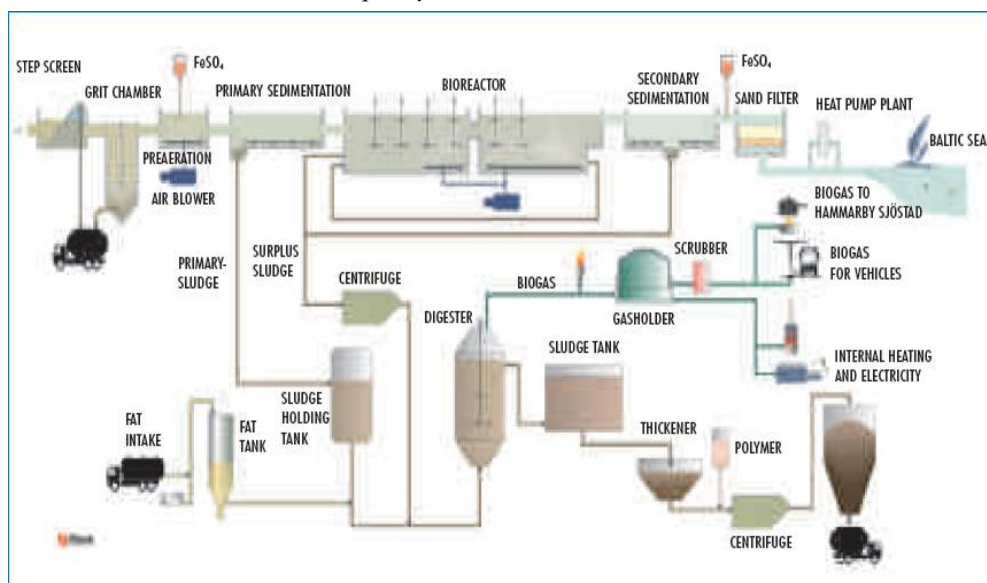


Fig. 10. Flowchart of Henriksdal WWTP processes (Source: Stockholm Vatten).

To target direct oxidation of persistent organic compounds, KMnO_4 application may be better applied after secondary sedimentation process, with or after the second FeSO_4 treatment. The benefit of application after biological process is that less KMnO_4 needs to be added since the COD concentration after activated sludge is much lower. Plus, the treated water at this stage should be much cleaner (almost free of suspended solids) that KMnO_4 oxidation should perform more effectively. Moreover, the in situ formed MnO_2 may be used and integrated with the sand bed to allow biological degradation of the oxidized organic compounds.

It is known that MnO_2 does have regenerative adsorption capability in bed bioreactor. Since KMnO_4 is reduced to MnO_2 , it will be interesting to study if the in situ MnO_2 produced would also have the regenerative capability like the mineral MnO_2 . If so, it may become a potentially more cost-effective treatment where the MnO_2 -bound flocs/sludge produced from the KMnO_4 oxidation could actually be used in a bed bioreactor to further degrade the oxidized organic compounds.

Based on these potentials, other than for regular wastewater treatment application, the utilization of these manganese compounds may potentially also be developed for decentralized wastewater treatment units that can help to purify and reuse the sewage water in remote areas.

With environmental concerns in mind, the fate of these manganese compounds following their applications may be described as follows:

- If KMnO_4 is added in another tank before biological process and done in very acidic pH, Mn^{2+} will be produced and but may be partially oxidized to Mn^{3+} or Mn^{4+} at the biological reactor where there is aeration. In any case, Mn^{2+} is soluble and will go throughout the WWTP processes and could get released to Baltic Sea. The oxidized manganese compounds are usually solids and may get retained during flocculation or sand filtration. However, implementing this KMnO_4 treatment also create another issue since pH adjustment needs to be done before the acidic water can go to biological tank, otherwise the biomass would be killed.
- If KMnO_4 is applied after secondary sedimentation together with or after FeSO_4 addition and if pH is neutral/leaning toward alkaline, then KMnO_4 is reduced to MnO_2 , and get retained in the sand filter where it can utilize its catalytic function. In this case, MnO_2 will be removed from time to time as sludge.
- If mineral MnO_2 is applied to the sand filter, its fate is similar to scenario 2 that it will remain there until it is disposed of as sludge.

Economically, in general, the price of KMnO_4 is more expensive since its production must be derived from MnO_2 . However, to determine how much the concentrations needed to give efficient removal (therefore actual cost) is beyond the scope of this study.

6. CONCLUSIONS

From literature reviews, the following conclusions can be made:

- Oxidation potential of MnO_2 and KMnO_4 is directly related to pH and that low pH is necessary for complete reduction of these manganese compounds to Mn^{2+} .
- The presence of other metal ions inhibits the oxidation process by MnO_2

- Applied in bioreactor bed, MnO₂ has regenerative property.
- KMnO₄ is a stronger oxidant than MnO₂ that can increase the biodegradability of persistent organic compounds.
- The presence of ligands can enhance KMnO₄ oxidation.
- MnO₂ and KMnO₄ can effectively remove phenolic compounds.
- On-going researches on the use of MnO₂ and KMnO₄ are focused on these compounds' efficiency in oxidizing specific organic compound.
- Each organic compound reacts and behaves differently upon its contact with MnO₂ and KMnO₄; therefore extensive studies need to be done if effective removal of all PPCP and EDC target compounds is desired.

From experimental results the following conclusions can be made:

- KMnO₄ is a strong oxidant that is not quite effective when applied in wastewater with high concentration of suspended solids (SS) as it reduces or masks its capability to oxidize soluble organic compounds (SCOD). Moreover, the presence of KMnO₄ actually eradicates biomass which may be important for biological treatment processes. Therefore KMnO₄ application is better be done in low SS water.
- MnO₂ efficiency on the application of wastewater containing high SS concentration is not affected, given there is high amount of MnO₂ and the contact period does not exceed 1 day (the boundaries of this thesis).
- MnO₂ application in a stirred reactor cannot be mixed with the presence of other flocculants as metal ions occupy the oxides active sites and inhibit the efficiency of oxidation by MnO₂.
- KMnO₄ application in a stirred reactor can be mixed with the presence of other flocculants and may enhance the oxidation potential of KMnO₄ itself and the overall flocculation process.
- Under the same experimental duration (4 hours), KMnO₄ was able to remove more TCOD and SCOD of supernatant than MnO₂ was. It indicates that KMnO₄ has a stronger oxidation potential and may be more effective in removing and/or enhancing the biodegradability of PPCPs and EDCs.

Overall, from both literature and laboratory studies, MnO₂ and KMnO₄ are potential and can be used to remove specific organic substances as well as COD from wastewater. However for an effective removal, certain parameters need to be considered, such as pH, the presence of other ions, suspended solids, as well as the type of reactants. Their application in wastewater treatment plants to help increase the water quality suitable for reuse is promising, especially through MnO₂ treatment in sand filter bed, KMnO₄ application at post-treatment to remove residual COD, and KMnO₄ oxidation – Mg-Ca flocculation to improve pre-treatment process.

7. RECOMMENDATION FOR FUTURE RESEARCH

In a smaller context, this study has served as a starting point to investigate the use of manganese compounds to respond the challenges in water resource management to remove PPCPs and EDCs from water. Below are suggestions for further follow-up research on the use of manganese compounds in wastewater treatment process:

- A study to examine the efficiency of MnO₂ and KMnO₄ in different stages of WWTP processes, preferably the ones closer to the end, where water has low SS and contains recalcitrant organic compounds.
- A study to examine the effect of pH on the oxidation potentials of these manganese compounds in removing COD, especially considering the interest to apply this chemical treatment in one of the WWTP step process.
- A study to test the biodegradability of the oxidized organic compounds following the oxidation by these manganese compounds (by BOD or oxygen uptake rate).
- A study of continuous sampling time to see the effect of oxidation over time.
- A study to compare the efficiency and regenerative property of MnO₂ oxidation potential in continuously stirred tank reactor and sand bed.
- A study of different KMnO₄ dose applications. (Note: to remove the intense color that can affect spectrophotometer reading, hydroxylamine hydrochloride or HNO₃.HCl as used by Aleboye *et al* (2009) may be needed to decolorize KMnO₄ solution)
- A study to design and test the efficiency of MnO₂ and/or KMnO₄ application in single decentralized wastewater treatment unit.

In a broader context, this master's thesis work has indicated a large potential for combining oxidation, adsorption and precipitation in one stage to improve typical western wastewater treatment and also to serve as a part of wastewater reuse, for instance for use as potable water. This combination process can provide alternatives and/or additions to common advanced wastewater treatment designs in Sweden as well as other western countries that typically use biological and chemical treatments for BOD, phosphorus and nitrogen removals; along with chemical (by the way of adsorption and oxidation) and membrane filtration (separation) for pathogens and pharmaceuticals removals. In addition, the combined use of oxidation, adsorption and precipitation can easily be installed in existing plants and incorporated in newly planned plants since it may be more advantageous than traditional design. A wide range of possibilities exists exemplified below:

- The combined use of permanganate and magnesium compounds (oxidation by permanganate, oxidation and adsorption by formed manganese dioxide, precipitation by magnesium compounds).
- The addition of ferrate (oxidation and precipitation by formed ferric compounds).
- The addition of magnetite or ferrous and ferric compounds (adsorption of phosphate and organic compounds, precipitation, and special possibilities for magnetic separation).
- The addition of manganese dioxide (biological oxidation including anaerobic nitrification, catalytic oxidation, and adsorption).
- The use of iron bacteria (adsorption, precipitation and possible oxidation of organics due to biologically produced hydrogen peroxide).

These different possibilities should then be evaluated based on treatment efficiency, energy consumption, costs, possibilities for reuse and chemical recovery, and solids handling and use.

8. REFERENCES

- Aleboyeh, A., Olya, M.E., Aleboyeh, H. 2009. Oxidative treatment of azo dyes in aqueous solution by potassium permanganate. *Journal of Hazardous Materials*. **162**:1530-1535.
- Alsheyab, M.A., Munoz, A.H. 2007. Comparative study of ozone and MnO₂/O₃ effects on the elimination of TOC and COD of raw water at the Valmayor station. *Desalination*. **207**:179-183.
- Andreozzi, R., Insola, A., Caprio, V., Marotta, R., Tufano, V. 1996. The use of manganese dioxide as a heterogenous catalyst for oxalic acid ozonation in aqueous solution. *Applied Catalysis A: General*. **138**:75-81.
- Balcioglu, I.A., Ötoker, M. 2003. Treatment of pharmaceutical wastewater containing antibiotics by O₃ and O₃/H₂O₂ processes. *Chemosphere*. **50**: 85-95.
- Balest, L., Lopez, A., Mascolo, G., Di Iaconi, C. 2008. Removal of endocrine disrupter compounds from municipals wastewater using an aerobic granular biomass reactor. *Biochemical Engineering Journal*. **41**: 288-294.
- Bendz, D., Paxeus, N.A., Ginn, T.R., Loge, F.J. 2005. Occurrence and fate of pharmaceutically active compounds in the environment, a case study: Höje River in Sweden. *Journal of Hazardous Materials*. **122**: 195-204.
- Birkett, J.W., Lester, J.N. 2003. Endocrine disrupters in wastewater and sludge treatment processes. *IWA Publishing Lewis Publishers, ch 6-7*.
- Carballa, M., Omil, F., Lema, J.M., Llompert, M., Garcia-Jares, C., Rodriguez, I., Gomez, M., Ternes, T. 2004. Behavior of pharmaceuticals, cosmetics, and hormones in a sewage treatment plant. *Water Research*. **38**:2918-2926.
- Carballa, M., Manterola, G., Larrea, L., Ternes, T., Omil, F., Lema, J.M. 2007. Influence of ozone pre-trt on sludge anaerobic digestion: removal of pharmaceuticals and personal care products. *Chemosphere*. **67**: 1444-1452.
- Carlsson, C., Johansson, A.K., Alvan, G., Bergman, K., Kühler, T. 2006. Are pharmaceuticals potent environmental pollutants? Part I: Environmental risk assessments of selected active pharmaceutical ingredients. *Science of the Total Environment*. **364**: 67-87.
- Colborn, T., Vom Saal, F.S., Soto, A.M. 1993. Developmental effects of endocrine-disrupting chemicals in wildlife and humans. *Environmental Health Perspectives*. **101**:378-384.
- Crossgrove, J., Zheng, W. 2004. Manganese toxicity upon overexposure. *NMR Biomed*. **17**:544-553.
- De Rudder, J., Van de Wiele, T., Dhooze, W., Comhaire, F., Verstraete, W. 2004. Advanced water treatment with manganese oxide for the removal of 17 α -ethynylestradiol (EE2). *Water Research*. **38**:184-192.
- Ellis, J.B. 2006. Pharmaceutical and personal care products (PPCPs) in urban receiving waters. *Environmental Pollution*. **144**:184-189.
- Esplugas, S., Bila, D.M., Krause, L.G.T., Dezotti, M. 2007. Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *Journal of Hazardous Materials*. **149**:631-642.
- EPA. 1999. Alternatives disinfectants and oxidants guidance manual. *EPA 815-R-99-014*. 346 p.

- Forrez, I., Carballa, M., Noppe, H., De Brabander, H., Boon, N., Verstraete, W. 2009. Influence of manganese and ammonium oxidation on the removal of 17 α -ethinylestradiol (EE2). *Water Research*. **43**:77-86.
- Galvin, R.M., Mellado, J.M.R. 1998. Potassium permanganate as pre-oxidant in a reverse osmosis water plant. *Water SA*. **24**(4):361-364.
- Gentili, A., Hendratna, A., Nilsson, M., Panagiotis, P., Tai, X.H. 2008. Wastewater treatment to reach drinking water quality. *Water and Waste Handling Course (AE 2301) Project, Department of Land and Water Resources Engineering, KTH*.
- Halling-Sørensen, B., Nors Nielsen, S., Lanzky, P.F., Ingerslev, F., Holten Lützhøft, H.C., Jørgensen, S.E. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. *Chemosphere*. **36**(2):357-293.
- Huber, M.M., Canonica, S., Park, G., Von Gunten, U. 2003. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ. Sci. Technol.* **37**:1016-1024.
- Jiang, J.Q., Yin, Q., Zhou, J.L., Pearce, P. 2005. Occurrence and treatment trials of endocrine disrupting chemicals (EDCs) in wastewaters. *Chemosphere*. **61**: 544-550.
- Jiang, J., Pang, S., Ma, J. 2009. Oxidation of triclosan by permanganate (Mn(VII)): Importance of ligands and in situ formed manganese oxides. *Environ. Sci. Technol.* **43**:8326-8331.
- Kulik, N., Trapido, M., Goi, A., Veressinina, Y., Munter, R. 2008. Combined chemical treatment of pharmaceutical effluents from medical ointment production. *Chemosphere*. **70**:1525-1531.
- Lin, K., Liu, W., Gan, J. 2009. Oxidative removal of bisphenol A by manganese dioxide: efficacy, products, and pathways. *Environ. Sci. Tech.* **43**:3860-3864.
- Lindberg, R.H., Wennberg, P., Johansson, M.I., Tysklind, M., Andersson, B.A.V. 2005. Screening of human antibiotic substances and determination of weekly mass flows in five sewage treatment plants in Sweden. *Environmental Science and Technology*. **39**(10):3421-3429.
- Lindberg, R.H., Björklund, K., Rendahl, P., Johansson, M.I., Tysklind, M., Andersson, B.A.V. 2007. Environmental risk assessment of antibiotics in the Swedish environment with emphasis on sewage treatment plants. *Water Research*. **41**: 613-619.
- Liu, R., Liu, H., Zhao, X., Qu, J., Zhang, R. 2010. Treatment of dye wastewater with permanganate oxidation and in situ formed manganese dioxides adsorption: cation blue as model pollutant. *Journal of Hazardous Materials*. **176**:926-931.
- Martins, R.C.C., Leal, H.M., Quinta-Ferreira, R.M.O. 2007. Catalytic removal of phenolic compounds by ozone using manganese and cerium oxides. *Proceedings of the World Congress on Engineering and Computer Science October 24-26, San Francisco, USA*.
- Mi, L. 2009. New possibilities of magnesium utilization in wastewater treatment and nutrients recovery. *TRITA-LWR Degree Project ISSN 1651-064X, LWR-EX-09-29*.
- Nelson, M.D., Parker, B.L., Al, T.A., Cherry, J.A., Loomer, D. 2001. Geochemical reactions resulting from in situ oxidation of PCE-DNAPL by KMnO₄ in sandy aquifer. *Environ. Sci. Technol.* **35**(6):1266-1275.
- Richardson, M.L., Bowron, J.M. 1985. The fate of pharmaceutical chemicals in the aquatic environment. *J. Pharm. Pharmacol.* **37**:1-12.

- San Sebastian Martinez, N., Fernandez, J.F., Segura, X.F., Ferrer, A.S. 2003. Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent. *Journal of Hazardous Materials*. **B101**: 315-322.
- Semerjian, L., Ayoub, G.M. 2001. High-pH-magnesium coagulation-flocculation in wastewater treatment. *Advances in Environmental Research*. **7**:389-403.
- Snyder, S.A., Adham, S., Redding, A.M., Cannon, F.S., DeCarolis, J., Openheimer, J., Wert, E.C., Yoon, Y. 2007. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination*. **202**:156-181.
- Stamatelatou, K., Frouda, C., Fountoulakis, M.S., Drillia, P., Kornaros, M., Lyberatos, G. 2003. Pharmaceuticals and health care products in wastewater effluents: the example of carbamazepine. *Water Science and Technology: Water Supply*. **13**(4):131-137.
- Stockholm Vatten. 2004. *Henriksdal Reningsverk brochure*.
- Stumm, W., Morgan, J.J. (1996) Aquatic Chemistry – Chemical equilibria and rates in natural waters, 3rd ed. *Wiley-Interscience Publications*. 1022 p.
- Suarez, S., Carballa, M., Omil, F., Lema, J.M. 2008. How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters? *Rev Environ. Sci. Biotechnol*. **7**:125-138.
- Suarez, S., Lema, J.M., Omil, F. 2009. Pre-treatment of hospital wastewater by coagulation-flocculation and flotation. *Bioresource Technology*. **100**: 2138-2146.
- SWITCH. 2007. Pharmaceutical compounds in environment. *Deliverable D 4.1.2 R A*
- Tekin, H., Bilkay, O., Ataberk, S.S., Balta, T.H., Ceribasi, I.H., Sanin, F.D., Dilek, F.B., Yetis, U. 2006. Fenton oxidation to improve the biodegradability of pharmaceutical wastewater. *Journal of Hazardous Materials*. **B136**:258-265.
- Ternes, T.A. 1998. Occurrence of drugs in German sewage treatment plants and rivers. *Water Resource*. **32**(11):3245-3260.
- Ternes, T.A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H., Haist-Gulde, B., Preuss, G., Wilme, U., Zulei-Seibert, N. 2002. Removal of pharmaceuticals during drinking water treatment. *Environ. Sci. Technol*. **36**:3855-3863.
- Tong, S., Liu, W., Leng, W., Zhang, Q. 2003. Characteristics of MnO₂ catalytic ozonation of sulfosalicylic acid and propionic acid in water. *Chemosphere*. **50**:1359-1364.
- UN-Water. 2007. Coping with water scarcity – challenge of the twenty-first century.
- Waddell, J.P., Mayer, G.C. 2003. Effects of Fenton's reagent and potassium permanganate applications on indigenous subsurface microbiota: a literature review. *Proceedings of the Georgia Water Resources Conference 23-24 April 2003*.
- Webb, S., Ternes, T., Gibert, M., Olejniczak, K. 2003. Indirect human exposure to pharmaceuticals via drinking water. *Toxicology Letters*. **142**: 157-167.
- WHO. 1981. Manganese: environmental health criteria 17. *UNEP, ILO, WHO*. 89 p.

Xia, K., Bhandari, A., Das, K., Pillar, G. 2005. Occurrence and fate of pharmaceuticals and personal care products (PPCPs) in biosolids. *J. Environ. Qual.* **34**:91-104.

**9. APPENDIX I – DATA FROM PRELIMINARY EXPERIMENTS:
SCOD AND DOC VALUES OF DIFFERENT TYPES OF
WASTEWATER BEFORE AND AFTER TREATMENTS**

Water type	Treatment	pH	SCOD t=0 (mg/L)	SCOD (mg/L)	DOC t=0 (mg/L)	DOC (mg/L)
Supernatant Bromma + 10% sludge	MnO ₂ – 7 days	8.1	525	364.5	489	872
	MnO ₂ – 14 days	8.1	525	417	489	855
	KMnO ₄ – 7 days	8.2	525	-	489	993
	KMnO ₄ – 14 days	8.2	525	-	489	1007
Effluent Hammarby SV line 1 (activated sludge) + 10% (v/v) sludge	MnO ₂ – 3 hours	6.6	101	44.6	97.1	42.5
	MnO ₂ – 24 hours	6.6	101	44.8	97.1	61.2
	KMnO ₄ – 3 hours	7.3	101	-	97.1	145
	KMnO ₄ – 24 hours	7.3	101	-	97.1	112
Influent Henriksdal + 10% (v/v) sludge	MnO ₂ – 3 hours	7.4	180	129	84	-
	MnO ₂ – 24 hours	7.4	180	100	84	60.6
	KMnO ₄ – 3 hours	8.0	180	185	84	-
	KMnO ₄ – 24 hours	8.0	180	308	84	127
Effluent Hammarby SV line 1 (activated sludge) + 30% (v/v) sludge	MnO ₂ – 3 hours	6.6	51.4	45.9	35	-
	MnO ₂ – 24 hours	6.6	51.4	51.5	35	41.4
	KMnO ₄ – 3 hours	7.0	51.4	105	35	-
	KMnO ₄ – 24 hours	7.0	51.4	>180	35	115

10. APPENDIX II – TCOD AND SCOD VALUES OF WASTEWATER BEFORE AND AFTER TREATMENTS

Water type	Treatment	pH	TCOD t=0 (mg/L)	TCOD rep 1 (mg/L)	TCOD rep 2 (mg/L)	SCOD t=0 (mg/L)	SCOD rep 1 (mg/L)	SCOD rep 2 (mg/L)
Unfiltered Influent <u>Henriksdal</u>	MnO ₂ – 4 hours	8.3	432	246	248	183	148	120
	MnO ₂ – 24 hours	8.3	432	172	162	183	98.5	98.4
	MnO ₂ –4 hr + flocculation	10.7	226	118	131	136	108	87.3
	MnO ₂ + flocculation	10.7	226	137	-	136	132	-
	KMnO ₄ – 4 hours	8.2	309	152	144	143	139	139
	KMnO ₄ – 24 hours	8.2	309	163	157	143	148	145
	KMnO ₄ –4 hr + flocculation	10.7	309	151	148	143	156	137
	KMnO ₄ + flocculation	10.7	309	127	-	143	124	-
	Mg-Ca flocculation	10.6	565	342	358	234	217	219
Unfiltered Supernatant <u>Bromma</u>	MnO ₂ – 4 hours	8.0	630	497	-	383	355	-
	KMnO ₄ – 4 hours	8.0	630	383	-	383	338	-
Filtered Supernatant <u>Bromma</u>	MnO ₂ – 4 hours	7.5	-	-	-	536	516	-
	KMnO ₄ –4 hours	7.5	-	-	-	536	483	-

11. APPENDIX III – THE EFFECT OF MnO_2 AND $KMnO_4$ APPLICATION IN THE PRESENCE OF SUSPENDED SOLIDS

The result of $KMnO_4$ application in section 4.2.1 caused the increase of SCOD concentration in the flask. However their increase was quite small, it was as small as the SCOD reduction at 4 hour treatment. Therefore, it was difficult to conclude if $KMnO_4$ did not remove SCOD at all or if it did but it was masked by $KMnO_4$ effectiveness in breaking down and solubilizing the suspended solids. Section 4.2.2 showed that in soluble supernatant, $KMnO_4$ seemed to be able to remove more COD than MnO_2 did. The presented data from preliminary experiments of this study support the notion that indeed $KMnO_4$ can cause the increase of both COD and TOC in the presence of suspended solids or biomass (Fig. 11).

In the preliminary experiments, $KMnO_4$ significantly added the COD and TOC concentration in the solution, which meant that there were some transformation and degradation of the organic particulates into soluble organic compounds. The different water samples used in the experiments (supernatant from Bromma WWTP, influent sewage water, and effluent from activated sludge of Hammarby Sjöstadverket) contained some portion of sludge which added the concentration of particulates/suspended solids of the water, which then got degraded and solubilized by $KMnO_4$. This finding showed that $KMnO_4$ is toxic for biomass and that the microorganisms could get eradicated in the presence of this strong oxidant. Similar findings were compiled and reported by Waddell and Mayer (2007) showing that $KMnO_4$ oxidation of organic contaminants actually may induce biodegradability as well as toxic effects to microorganisms. On the contrary, MnO_2 did not seem to pose the same destructive effect to biomass; its presence seemed to be tolerated since it was observed that COD and TOC could get positive removal. However, it might be true only for a certain length of reaction time since TOC addition was observed when the experiment was run for much longer time (7 and 14 days).

The series of the studies performed also might have indicated that $KMnO_4$ is efficient in oxidizing organic compounds in relatively short period of time after initial contact (within 1 hour as was the case explained in section 4.3.2). It might have been possible that after longer contact time (about 4 hours and more), hydrolysis could dominate the reaction that caused the dissolution of organic compounds.

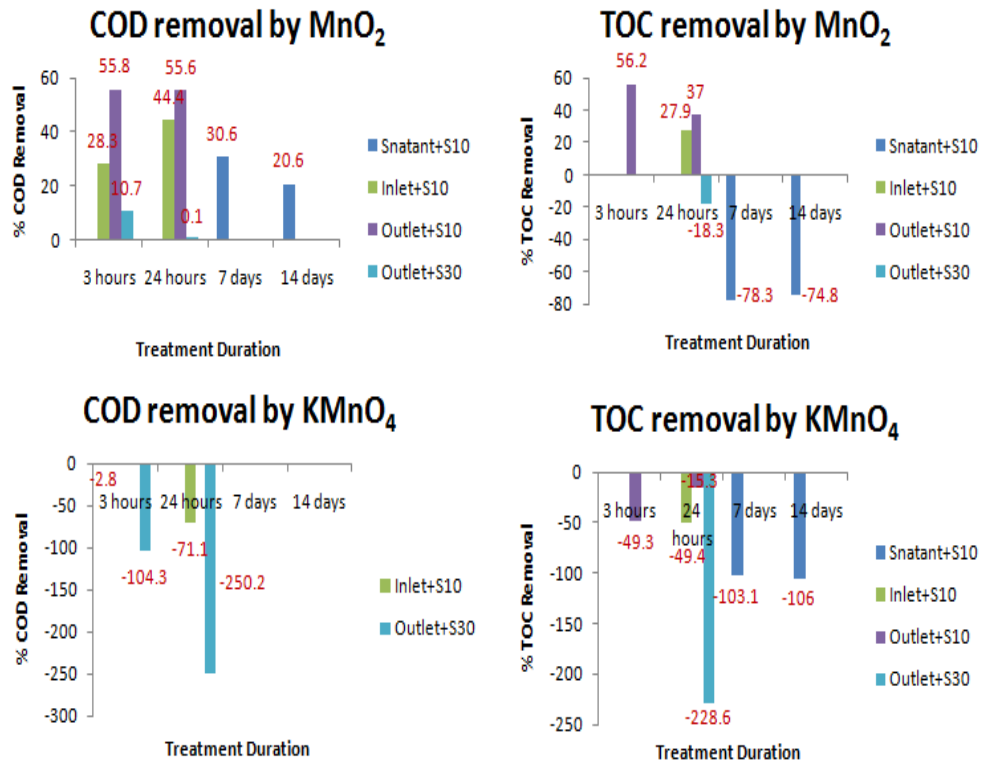


Fig. 11. COD and TOC removals by MnO₂ and KMnO₄ from various wastewater sources with the addition of sludge.

Legend:

Snatant+S10 = Bromma supernatant + sludge (10% volume)

Inlet+S10 = Henriksdal influent + sludge (10% volume)

Outlet+S10 = Henriksdal effluent from activated sludge + sludge (10% volume)

Outlet+S30 = Henriksdal effluent from activated sludge + sludge (30% volume)