Tampere University of Applied Sciences

Oxidation of Organic Compounds in Acidified Fresh Human Urine Using Fenton's Reagent

Focus on the removal of COD and recovery of nitrogen

Abdullah Al-Saadi

BACHELOR'S THESIS
June 2023

Environmental Engineering

ABSTRACT

Tampereen ammattikorkeakoulu
Tampere University of Applied Sciences
Environmental Engineering

Abdullah Al-Saadi
Oxidation of organic compounds in acidified fresh human urine using Fenton's reagent
Focus on the removal of COD and recovery of nitrogen

Bachelor's thesis 41 pages, appendices 1 page
June 2023

Urine is a nutrients-rich containing solution that can be retained and utilized for agricultural purposes. Unfortunately, it is considered a waste that is lost in the existing conventional wastewater treatment. Swedish University of Agricultural Sciences (SLU) has conducted technologies that concern the treatment of source-separated urine aiming to convert human urine to a green fertilizer.

However, this technology is limited due to the presence of high concentrations of organic compounds in urine, which obstruct the urine dehydration process to produce a solid fertilizer. This research aims to provide a practical solution for removing organic compounds from urine by using the Fenton reagent-based Advanced Oxidation Process (AOP).

The results of the study demonstrated an 80% removal in the Chemical Oxygen Demand (COD) from urine. Further analysis showed a 30% decrease in nitrogen concentration in urine after the treatment. The loss in nitrogen is attributed to the oxidation of chloride ions forming chloride radicals, that oxidise nitrogen compounds to nitrogen gas N_2 in a series of reactions. Moreover, phosphorus ions were found to react with ferrous/ferric iron, leading to the formation of iron phosphate (precipitate).

The outcomes of this research can be implemented to enhance urine treatment at SLU. Furthermore, this study contributes to Sustainable Development Goals 2, 3, and 6 in promoting food security, contributing to public health, and improving water sanitation.

Further research will be conducted to investigate the fate of pharmaceutical by-products found in the urine after the Fenton oxidation process. Another research project will also aim to enhance nitrogen and phosphorus recovery observed in this study.

Keywords: urine, wastewater, nutrients recycling, fertilizer, food security

CONTENTS

ABBREVIATIONS AND TERMS

TCOD: Total chemical oxygen demand

COD: Chemical oxygen demand

CF: Concentration factor

TON: Total oxidised nitrogen

TN: Total nitrogen

1 INTRODUCTION

Nutrient recycling has gained wide interest from recent technologies to understand how to sustain and preserve the nutrient cycle. (Jiaying et al., 2022) Nutrients such as nitrogen (N), phosphorus (P), and potassium (K) are essential in supporting plant growth and have a significant influence on the food chain. Unfortunately, the cycle of these nutrients is not closed, i.e., some are lost in the form of gas or complex compounds.

Wastewaters are nutrient-containing solutions that are ultimately discharged into the swage pipelines and eventually reach the existing conventional wastewater treatment, where valuable resources are being lost. Nitrogenous compounds are lost in the denitrification process of the treatment in the form of nitrogen gas (N_2). Precisely, the action of the nitrifying bacteria converts nitrate (NO_3) ions back to nitrogen (N_2) gas. (Wang and Chu, 2016) While phosphorus and potassium loss occur in the form of a sludge complex during the coagulation/flocculation process, using a chemical coagulant (e.g., aluminium sulfate). (López-Maldonado et al., 2014)

The loss of these nutrients not only poses a threat to the environment through eutrophication, but it also threatens the global food supply and nutrient sustainability. To address this challenge, it is important to seek an alternative method aiming to retain these nutrients and preserve their cycle.

Urine, one of the wastewater streams, contains a rich composition of essential nutrients that end up being lost during the current conventional treatment methods. On average, an individual excretes about 500 L of urine per year, which is equivalent to approximately 5.6 kg of nitrogen (N), 0.4 kg phosphorus (P), and 1 kg of potassium (K). However, urine composition and volume can vary among individuals depending on factors such as food diet, physical activity, body size, and environmental conditions. (Vinnerås, Jönsson, 2002)

Besides nutrients, urine excretes a high concentration of organic material with the measured Chemical Oxygen Demands (COD) of about (5 – 10) g/L. (Putnam,

1971) Including medicine residuals, and hormones, which cause severe contamination when they reach the environment. Drugs and pharmaceuticals ingested in the human body are consumed partially, and about 70% excrete during urination. (Özel Duygan et al., 2021)

The emerging approach of source separation of urine has been facilitated by the Swedish University of Agricultural Sciences SLU for several decades. Technologies concerned with sustainable nutrient recovery from urine, offer a solution to address the challenge of nutrient loss occurs. At SLU technology, the focus is to treat the urine separately to recover nutrients and produce fertilizer. Two commonly employed methods at SLU involve alkalization or acidification treatment of urine, followed by dehydration in a substates mixture (e.g., wheat bran and biochar) to produce a solid fertilizer. (Simha et al., 2020, Simha et al., 2023)

This technology currently faces a limitation due to the presence of a high concentration of COD in the final fertilizer. The high COD levels contribute to undesirable properties in the fertilizer, such as odour and hindered dehydration rates. To overcome this challenge, this research proposes the utilization of the Fenton reagent-based Advanced Oxidation Process (AOP) to remove COD effectively from acidified urine.

The study aims to investigate the optimal parameters of the Fenton reagent based AOP for achieving efficient COD removal in urine. This entails a comprehensive examination of some factors that influence the oxidation process such as the hydrogen peroxide dose, ferrous iron dose, pH condition, temperature, and reaction time. By optimizing the process parameters, this study intends to enhance the efficiency of urine treatment in the SLU technology to convert urine into hygienically safe fertilizer while addressing the COD issue.

It is important to note that this study specifically focuses on the Fenton oxidation process of organic compounds in urine, and it does not explore the dehydration process of the treated urine or conduct a pharmaceutical analysis. Further study is planned to examine the fate of pharmaceutical by-products in urine after applying the Fenton reagent-based Advanced Oxidation Process (AOP). Additionally,

another research project will aim to enhance nitrogen and phosphorus recovery observed in this study.

In the context of the Sustainable Development Goals (SDGs), this research contributes to several targets. First, by addressing the loss of nutrients in wastewater and promoting nutrient recovery to enhance food availability, this research supports SDG 2 (Zero Hunger) and aligns with SDG 6 (Clean Water and Sanitation), which seeks innovative wastewater treatment solutions that minimize environmental impact and preserve valuable resources.
By preserving the natural cycle of these nutrients, this research contributes to the transition toward a circular economy in wastewater management. Lastly, by investigating the removal of pharmaceuticals, this research contributes to SDG 3 (Good Health and Well-being) by addressing the potential risks associated with pharmaceutical residues in the environment. (THE 17 GOALS | Sustainable Development, n.d.)

2 Theory

2.1 Human urine composition

Human urine comprises about 95 % water and 5 % dissolved solids (organic and inorganic compounds), which are the end-products of various functions occurring in the human body. (Putnam, 1971) These compounds are classified as nitrogenous, hormones, vitamins, organic acids, and other compounds.

The main organic compounds found in human urine are urea (CH_4N_2O), creatinine ($C_4H_7N_3O$), creatine ($C_4H_9N_3O_2$), citric acid ($C_6H_8O_7$), Glucuronic acid ($C_6H_{10}O_7$), and organic ammonium salts. Urea contributes to 80% of the total nitrogen in urine.
Dominant inorganic salts are sodium phosphate (NaH_2PO_4), potassium chloride (KCl), sodium chloride (NaCl), and potassium sulfate (K_2SO_4). The rest are low concentrations of organic acids and inorganic salts, as seen in Tables (1 and 2).

TABLE 1. Organic compounds in human urine at a concentration > 0.1 g/L. (Putnam, 1971)

Name	Molecular weight g/mole	Concentration in urine, mean g/L	Solubility in H2O g/L
Urea	60.1	16.3	545
Creatinine	113.12	1.5	80.1
Citric acid	192.12	0.51	592
Glucuronic acid	194.14	0.475	Missing
Tyrosine	181.19	0.381	0.453
Creatine	131.13	0.373	13.3
Uric acid	168.11	0.355	0.06
Glycine	75.07	0.315	249
Phenol	94.11	0.292	82.8
Histidine	155.15	0.233	45.6
Lactic acid	90.08	0.215	1000
Glutamic acid	147.13	0.195	8.57
Androsterone	290.4	0.174	0.0012
1-Methyl-L-histidine	169.18	0.173	Missing
beta-D-Glucose pentaacetate	390.34	0.156	1.5
Imidazole	68.1	0.143	663
Taurine	125.15	0.138	94.9
Aspartic acid	133.1	0.12	5.39

TABLE 2. Inorganic salts in human urine with a concentration > 0.05 g/L. (Putnam, 1971)

Name	Concentration in urine (mean) g/L
Sodium Chloride	8.001
Potassium Chloride	1.641
Potassium Sulfate	2.632
Magnesium Sulfate	0.783
Sodium phosphate	0.6
Magnesium Carbonate	0.143
Potassium Bicarbonate	0.661
Potassium Phosphate	0.234
Calcium Phosphate	0.062

The approximate pH value of human urine is around 7 and holds a COD value between 5 - 10 g/L, and 7 g/L is the average value. (Putnam, 1971) Human urine is recognized due to its yellow colour, which belongs to the pigment urochrome or urobilin. The more concentrated urine is the darker colour it gets. A healthy person excretes an average amount of 1.5 litres of urine per day. Additionally, urine holds concentrations of residual antibiotics, hormone drugs, and pharmaceuticals, which are considered the major contaminants in water pollution. (Li et al., 2023)

2.1.0 Urine Treatment to produce fertilizer

Treatments involve the recovery of nitrogen, potassium, and phosphorus, other nutrients found in urine to produce fertilizer. Treating urine is beneficial in many perspectives, besides recovering nutrients, water can be recovered as well. Nutrient recovery from urine can be a greener route for fertiliser production than the typical way, the Haber Bosch process, which demands high energy. (Haber-Bosch Process, n.d.) Also, treating urine separately limits the fate of pharmaceuticals and prevents them from reaching the environment.

To produce safely hygienic fertilizer, urine must undergo either physiochemical or biological treatments under certain conditions. Treatments aim to achieve the removal of contaminants such as pharmaceuticals by-products excreting with urine. It also involves oxidation of organic compounds with preserving nitrogen (urea).

Urine contains mostly water, which can be removed by applying a dehydration treatment aiming to produce a solid fertilizer. The urine concentration factor (Cf) is calculated as the mass ratio of the urine add (g) to the urine remaining (g) after drying, as shown in equation (1). (Simha et al., 2022)

$$Cf = \frac{Urine\ mass\ added\ (grams)}{Urine\ mass\ remained\ (grams)} \qquad (1)$$

Globally, there are many technologies concerning urine treatment to produce safe fertilizer. At the Swedish University of agriculture sciences, nutrient recovery from urine is done through alkalizing/acidifying, then dehydrating the urine to produce a solid fertilizer. The alkalization process produces a fertilizer with a capacity of 10% N, 1% P, and 4% K. (Simha et al., 2020) At which, urine is alkalized to pH ≥ 10 using magnesium oxide MgO then dehydrated at 50 °C in a substate mixture containing biochar and wheat bran.

While in the treatment of acidifying the urine using either organic (citric acid) or inorganic (sulfuric acid) acids then drying it at an ambient temperature (20°C ± 2). This treatment yielded a solid fertilizer with a nutrient capacity of 17.9–21.2 % nitrogen, 1.1–3.6 % phosphorus, 4.2–5.6 % potassium, and 15.4–19.4 % carbon. (Simha et al., 2023) The obstacle in the alkalization urine treatment is the formed calcite during the process while in the acidification treatment, no calcite formation occurs.

The aim of stabilizing urine under basic or acidic conditions is to prevent urea hydrolysis, which is caused by urease enzymes, that are found naturally in human urine and the surrounding environment. Urease enzymes are activated at pH conditions ranging between 5 and 9. It hydrolyse urea into total ammonium nitrogen TAN= (NH_3 + NH_4^+) and carbonic acid. The formation of ammonium ions or ammonia shifts the urine pH from near neutral to ≥ 9. Thus, to preserve urea, urine

must be alkalized to a pH of ≥ 10 or acidified to a pH of < 4 before the dehydration process. (Simha et al., 2023)

SLU has conducted further investigation into the inactivation of pathogens in alkalizing/dehydrating urine treatment which stated, that drying the urine under basic conditions (pH ≥ 10) led to the inactivation of several microorganisms such as Ascaris suum, Enterococcus faecalis, bacteriophages MS2, ΦX 174 and salmonella app. (Senecal et al., 2018)

Furthermore, urine treatment can be done through a nitrification process, in which urine is treated biologically to produce fertilizer. This treatment is done in a biofilm reactor as follows; urea is first hydrolysed by urease enzymes to produce TAN ($NH_3 + NH_4^+$), which is then oxidized into nitrite NO_2 and then into nitrate NO_3 by nitrifying bacteria. This process is done under aerobic conditions at a sensitive pH range between 7 and 8. (Tarre & Green, 2004) Additionally, this treatment is combined with a filtration process, utilizing a granular activated carbon filter for the sake of micropollutants removal from nitrified urine. (Özel Duygan et al., 2021) Applying this treatment, produces a high-nutrient solution that can be used for agricultural practices.

Physical urine treatment is done through membrane filtration processes such as the two-step process of forward osmosis and membrane distillation. (Ray et al., 2019) Other combined treatments, hybrid nanofiltration, and reverse osmosis processes. (Courtney & Randall, 2022)

2.1.1 The Removal of organic compounds from human urine

Human urine excretes various types of organic compound complexes, as seen in Table (1). Also, it is shown in Figure (1), urea and creatinine compounds are the major organic compounds in urine. The remaining organics are classified as, amino acids and organic acids.
Organic compounds are removed from urine for many reasons: They affect the water activity thus obstructing the evaporation rate, they inhibit the degradation

of the micropollutants (e.g., during UV treatment), and add undesired smell to the final fertilizer.

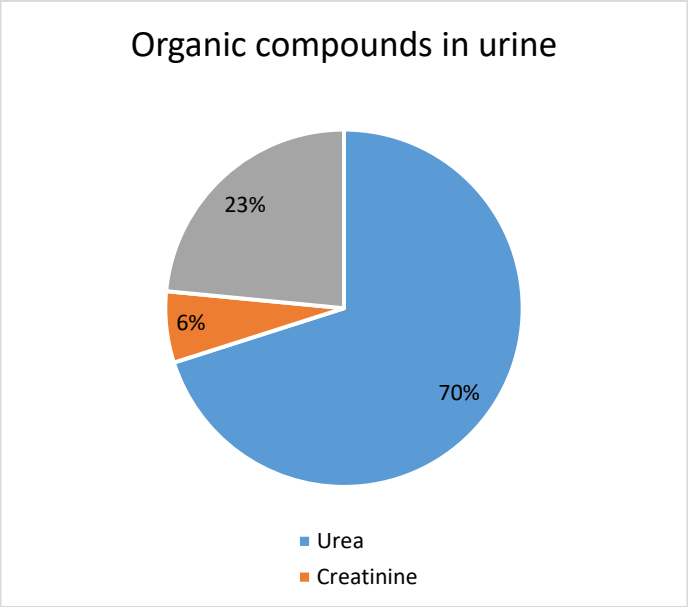


FIGURE 1. Shows the major organic compounds in human urine. (Putnam, 1971)

These organics are degraded in several pathways chemically or physically. Chemical degradation is referred to oxidation methods (e.g., Fenton AOPs, ozonation, chlorination), that involve electron transformation (losing electron). (Lee, Shoda, 2008, Ozone Used for COD Reduction in Wastewater – Oxidation Technologies News, n.d.)

Physical treatments refer to nanofiltration using membrane technologies as well as granular active carbon filtration processes. (Köpping et al., 2020)

2.2 Fenton's Regent-based Advanced Oxidation Process

Fenton's reagent-based advanced oxidation process was invented in 1894 by the chemist Henry John Horstman and followed by further discussions and studies by Haber, F. and Weiss, J. Barb, W.G. et al. (Arsene & Gorinchioy, 2019) The process involve the formation of the reactive specie hydroxyl radical •OH, that occurs when mixing hydrogen peroxide solution and an iron solution containing ferrous (Fe^{2+}) in an acidic medium.

Hydroxyl radical •OH oxidizes organics to form end-products of CO_2, water, and inorganic salts (if inorganics are present in the influent). The standard redox potential of the hydrogen peroxide is 1.8 V, while the hydroxyl radical is 2.8 V at the standard hydrogen electrode. (Hydrogen Peroxide, n.d.) Fenton AOP is widely used in water sanitation systems for COD/BOD removal. (Lee, Shoda, 2008)
It is one of the most effective disinfecting methods against germs and microbes. This process is usually followed by an additional filtration treatment such as a granular activated carbon filter.

In Fenton's reagent, ferrous ions Fe^{2+} activate hydrogen peroxide, forming hydroxyl radicals •OH. The reaction continues to regenerate the ferrous ions (Fe^{2+}). (Xu et al., 2020) In the first phase of the reaction, the ferrous ions are oxidized by the hydrogen peroxide to form ferric ions Fe^{3+} and hydroxyl radicals •OH and hydroxide ions OH^-, as shown in equation (2).
In the next phase of the reaction, ferric ions react with the hydrogen peroxide in a redox reaction to regenerate ferrous ions as well as forming secondary hydroxyl radicals $•HO_2$, and hydrogen ions H^+, as shown in equation (3).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + •OH + OH^- \qquad K1= 63.5\ M^{-1}.S^{-1} \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + •HO_2 + H^+ \qquad K2= 0.001–0.01\ M^{-1}.S^{-1} \qquad (3)$$

However, the second reaction is slower than the first reaction at about three-order magnitude. To initiate Fenton oxidation, it is important to determine the Fe (Catalyst)/H_2O_2(oxidant) molar ratio, pH condition, and mixing time. (Xu et al., 2020)

Another study done by Bray, W.C., and Gorin, M.H. suggests the formation of the active ferryl-oxo complex during Fenton's reagent-based oxidation process, (equations 4 and 5). (Arsene & Gorinchioy, 2019) Extensive studies followed to illustrate the mechanism of this reaction; However, no evidence could identify the intermediate formation due to the short lifetime of the reaction.

$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \qquad (4)$$

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + H_2O + O_2 \qquad (5)$$

The Fenton oxidation process is effective but has some obstacles, including chemical dose, a large formation of ferric oxide sludge during treatment, and demand for a strong acid to proceed with the reaction performance. (Pathania et al., 2020, Xu et al., 2020)

2.2.0 Optimal parameters

Evaluating the Fe:H_2O_2 molar ratio

The chemical dose of the ferrous ions to the hydrogen peroxide Fe:H_2O_2 is one of the limiting factors in the initiation of the hydroxyl radical •OH. Precisely, Ferrous iron Fe^{2+} is the limiting reactant in the Fenton reagent based AOP. Furthermore, the optimal dose of hydrogen peroxide H_2O_2 and ferrous ion Fe^{2+} depends on the type of the treated solution.

Since COD content characterizes the quality of water; domestic wastewater holds a COD value of about 2,000 mg/L, pharmaceutical wastewater has a high concentration of organic matter with a COD content ranging between 4,000 to 10,000 mg/L, whereas, in unpolluted surface water, the COD value is between 5 to 20 mg/L. (Ling et al., 2016, Shetty & Verma, 2015, *Sum Parameters: Potential and Limitations - ScienceDirect*, n.d.)

According to the legislation of the world health organization (WHO), the COD level of drinking water must not exceed 80 mg/L. (Olayinka et al., 2013)

Evaluating the Fenton's reagent-based AOP on pharmaceutical wastewater, it appeared that a dose of 900 mg/L of the hydrogen peroxide at a 1:3 Fe:H_2O_2 molar ratio has achieved a maximum COD removal of >90%. (Shetty & Verma, 2015) Landfills, present a large amount of organic carbon and nitrogen-containing compounds that end up in the leachate. To treat landfill leachate with the Fenton reagent AOP, a 1:1.5 Fe:H_2O_2 molar ratio is required. (Zhang et al., 2005) In the decolorization process, a 1:40 Fe:H_2O_2 molar ratio is the most applicable molar ratio. (Papić et al., 2009).

The difference between the mentioned wastewaters is the COD content and it appears that the ratio of the reactants Fe:H_2O_2 depends on the amount of the

TCOD (mg/L) as well as depending on the matrix type of organic and inorganic substances found in the treated wastewater.

Evaluating the pH condition

In most Fenton AOP literature, a pH condition of 2.8 is the optimal condition to achieve an effective oxidation treatment. (Saharan et al., 2014) This occurrence is strongly related to the dissociation of iron in an aqueous medium, at a pH condition just below 3 presenting both free ferrous Fe^{+2} and ferric Fe^{+3} ions. (Furcas et al., 2021)

At a pH value above 3, the ferrous ions are dissociated in another form of iron $Fe(OH)_2$ compounds (K-value = 586 $M^{-1}.s^{-1}$), which are 10 times more reactive than the ferrous ions Fe^{2+} (K-value = 40 - 80 $M^{-1}. s^{-1}$) at 0.1 M ionic strength and 25°C. (Pignatello et al., 2006)

Furthermore, at a pH value below 2.5, hydroxyl radicals are scavenged by the hydrogen ions ^{+}H forming water, leading to the degradation of hydrogen peroxide. At the same pH conditions, ferrous ions start to dissociate into $(Fe(II)(H_2O))^{+2}$, which is another form of ferrous ions, that reacts slower with hydrogen peroxide than the ferrous ions Fe^{2+}. (Saharan et al., 2014)

At higher pH conditions (I.e., Between 4.5 - 6), ferric iron Fe^{3+} that is formed in the first reaction (equation 2) undergoes a hydrolysis reaction and eventually precipitates as inactive iron salts, which are called Schwertmannite, ferrihydrite, and goethite. (Rose, 2010) This precipitate leads to the reduction of iron Fe^{3+} ions, thereby, inhibiting the regeneration of ferrous ions, interrupting the Fenton oxidation process. Additionally, the oxidation potential of the hydroxyl radical decreases at high pH conditions, at which it degrades to produce water and O_2. (Saharan et al., 2014)

2.2.1 Fenton oxidation of organic/inorganic compounds

The Oxidation process of organic and inorganic compounds in the Fenton reagent AOP belongs to the oxidative potential attack of the free hydroxyl radical

•OH. There is literature available on the rate constant (K-value) for the reaction between some organic compounds and the hydroxyl radicals, see table (3).

TABLE 3. Shows the oxidation capacity of the hydroxyl radical •OH against some organic/inorganic compounds. (Dorfman et al., 1973)

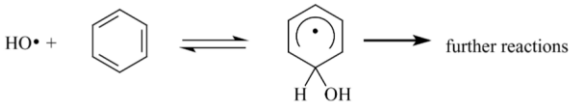
Compound	K-value $M^{-1}. s^{-1}$
Urea	7.9×10^{5}
Amino acids	$10^{7} – 10^{8}$
Carbohydrates	$10^{8} – 10^{10}$
Pharmaceuticals	$10^{9} – 10^{10}$
Simple peptides	$10^{7} – 10^{9}$
Chloride	4.3×10^{9}
Dioxane	2.4×10^{9}
A-dimethyl trimethyl acetamide	4.0×10^{9}

The reaction between the hydroxyl radical •OH and organic compounds targets the organic molecules' centre carbon, creating oxidizable carbon radicals R•. In other meaning, losing a hydrogen ion H from the chain of organic molecules C—H, N—H, O—H.

On the other hand, with double-bonded molecules C=C or aromatic rings, the hydroxyl radical is bonded to create further oxidizable radicals, as shown in equations (6, 7, and 8). (Pignatello et al., 2006)

$$\bullet OH + R—H \rightarrow H_2O + R\bullet \quad (6)$$

$$\bullet OH + C=C \rightarrow OH—C—C\bullet \quad (7)$$



(8)

Eventually, the end-product in the Fenton oxidation process of organics and inorganics leads to the formation of CO_2, H_2O, inorganic salts, and inorganic acids. (Pignatello et al., 2006)

2.2.2 The impact of inorganic compounds on Fenton reagent based AOP

Depending on the matrix of the treated wastewater, Fenton oxidation of organic compounds can be inhibited in the presence of some inorganic ions such as sulfate, phosphate, bromide, and chloride. Regarding the ionic concentration of these ions in the treated solution, the inhibition can be either scavenging the hydroxyl radical •OH, iron precipitation in the presence of phosphate to form iron (III) phosphate or vivianite, or the reaction between the hydrogen peroxide and the ferric ions Fe^{3+} to form less reactive iron species such as $Fe(HO_2)^{2+}$. (Pignatello et al., 2006)

In the presence of phosphorus ions, ferric ions Fe^{3+} formed in the second reaction (equation 3) tend to form a precipitate of iron (|||) phosphate.
Sulfate ions present in the wastewater have impacts on the Fenton oxidation process by coordinating ferric ions to bind with sulfate ions to form soluble iron complex $FeSO_4^+$ and $Fe(SO_4)_2^-$, which are unreactive with hydrogen peroxide H_2O_2. (Pignatello et al., 2006)
Halides, chloride Cl^- and bromide Br^- ions are found in wastewater at certain concentrations (For Cl^- above 0.01M at pH 2.8) inhibit the Fenton oxidation process by scavenging the formed hydroxyl radicals. Meaning, hydroxyl radicals tend to oxidize halide ions (Cl^- and Br^-) forming halide radicals, resulting in further oxidation stress against organics to form chlorinated by-products. (Clark et al., 2021)
Chlorate, perchlorate, organic and inorganic chloramines are chlorinated by-products that are considered hazardous environment compounds. Perchlorate is highly persistent in the environment and disturbs the thyroid gland production in the human body. (Perchlorates | Public Health Statement | ATSDR, n.d.) The oxidation of halides towards organic compounds occurs via H-abstraction or addition, as shown in equation (9). (Pignatello et al., 2006)

$$HO\bullet + X^- \rightleftharpoons HOX\bullet^- \ ^{(H+\,(-H2O))} \qquad (9)$$

In the case of H-abstraction, the end-product would be mineralization, whereas in H-addition forms organohalides compounds.

3 Methods

3.1.1 Materials

Chemicals used in the experiment were hydrogen peroxide 50 % (wt.) solution (VWR, Germany), Iron sulfate heptahydrate (Merck, Germany), Titanium (IV) oxysulfate – 27 – 31 % sulfuric acid hydrate reagent (Merck, France), Sulfuric acid 95 % solution (Merck, Germany). Other chemicals of analytical grade were 1M sodium hydroxide solution, 2 M citric acid solution, 1 M sulfuric acid, and oxalic acid.

Chemicals used to prepare the synthetic urine solutions are sodium phosphate monobasic dihydrate, sodium chloride, calcium chloride, potassium chloride, urea, sodium sulfate monohydrate, magnesium chloride hexahydrate, ammonium chloride, and 5 M potassium hydroxide solution. These common chemicals are of analytical grade.

3.1.2 Preparing ferrous iron Fe^{2+} stock solution

To prepare iron sulfate heptahydrate stock solution, 12.265 g of FeSO4.7H2O was dissolved in a flask containing 100 mL Milli-Q water. The Milli-Q water was pre-acidified to a pH condition of 2 by adding 95 % sulfuric acid. The solution was mixed for 15 minutes using a magnetic stirrer (101222013, VWR, USA) to allow iron dissolution (Becomes light green colour). The pH increased when the iron sulfate heptahydrate was added, thus it must be maintained again to a pH value of 2.
The flask beaker was kept closed during the mixing and storing phases using a cap to prevent the free oxidation of iron from Fe^{2+} to Fe^{3+} by O_2 gas found in the air (21 %).

3.1.3 Preparing synthetic urine

Synthetic urine was prepared at different concentration factors, Cf1, Cf5, and Cf10 by dissolving the measured salts that are shown in Appendix 1 (1) Table (4) in 1-liter milli-Q water using a glass bottle closed with a lid. The solution was mixed for 5 minutes using the magnetic stirrer.

3.1.4 Collecting and drying real urine

Fresh urine was collected daily in sterile high density of polypropylene bottles that were placed in three toilets in one of the SLU departments. Urine was collected from different genders aged 25-60 years at different times of the day. At the end of the day, the bottles were collected and poured into a 25-litre plastic container containing 37,5 g of the 95 % sulfuric acid solution, which was enough to acidify a total volume of 25-litre of urine to a pH value of 3. The urine was mixed after every time of urine addition using OHS-40 digital overhead stirrer (514997, VELP SCIENTIFICA, Italy).

The urine drying process to make concentrated urine was done in an incubator (DC4600HPWR, Electrolux, Sweden). First, the acidified urine was poured into a glass dish (Ikea, Sweden), which is then placed inside the incubator. During the drying process, urine was added to reach higher concentration factors. After reaching the desired concentration factor, the remaining urine including solid particles was collected inside a 1-litre glass bottle. Urine concentration factors Cf1, Cf5, and Cf10 were calculated by using equation (1).

3.2 Experimental procedure

The experiments were first conducted using synthetic urine, and later the focus was shifted toward real urine. The investigation had three objectives, first optimizing the Fe:H_2O_2 molar ratio of the catalyst iron sulfate heptahydrate to the oxidant hydrogen peroxide. Second, optimizing the pH value that suits the reaction, and third, kinetics evaluation of the reaction.

Fenton oxidation treatment was examined on three different urine concentration factors (Cf1, Cf5, and Cf10), and the measurements were done in duplicate. The pH condition of the reaction was adjusted using 1 M sulfuric acid/1 M sodium hydroxide. The mixing time of the reaction was carried out for 2 hours under room temperature (~ 22°C) and 1 atmospheric pressure. Before starting the oxidation process, urine samples of the concentration factors Cf5, and Cf10 were filtered by using 0.45 µm filters (17517489, Whatman, China).

The addition order of the reactants was performed by first, acidifying the urine, adding the hydrogen peroxide, then adding the ferrous iron solution, and finally pH adjustment.
In real urine, the hypothesis behind the study effect of the pH condition and the Fe:H_2O_2 molar ratio are supported with COD analysis to identify the activation pathway of the hydrogen peroxide against the removal of organic compounds (I.e., radical, or non-radical pathway).

3.2.0 Synthetic Urine

Evaluation of the Fe:H_2O_2 molar ratio
The first objective of this experiment was to examine the effect of the Fe:H_2O_2 molar ratio on the activation of the hydrogen peroxide (I.e., hydroxyl radical formation). The experiment started by first, acidifying the synthetic urine to pH 3 using the 2 M citric acid. The citric acid was used to provide organic compounds to the synthetic urine, which is containing about 4 grams of organic carbon. The second step is the addition of the oxidant and the catalyst by applying 1 g H_2O_2/L at three different Fe:H_2O_2 molar ratios of (1:5, 1:10, and 1:20).

Evaluation of the pH condition
The second objective of the experiment was to select the most suitable pH condition that gives the highest activation in the hydrogen peroxide. This experiment was done by acidifying the synthetic urine at three different pH values 2.5, 3, and 3.5 using 2M citric acid. Then, 1 g H_2O_2/L was applied at a fixed 1:5 Fe:H_2O_2 molar ratio.

Kinetic study

The third objective of the experiment was to evaluate the kinetics of the Fenton oxidation reaction in synthetic urine at selected interval reaction times while the pH was fixed at 3 (using 2M citric acid) and 1 g H2O2/L was added at a fixed 1:5 Fe:H_2O_2 molar ratio.

3.2.1 Real Urine

Evaluations of the Fe:H2O2 molar ratio and the pH conditions

In real urine, the experiment was carried out at the same parameters that were done on synthetic urine as well as using the same amount of hydrogen peroxide (1 g H2O2/L). Except, the acidification of the real urine was done using the 95 % sulfuric acid solution, and the study evaluation of the Fe:H_2O_2 molar ratio and the pH condition were only done on real urine Cf1.

The Fe:H_2O_2 molar ratio was studied with a wider range of 1:8, 1:4, 1:2, 1:1, and 1.5:1 at a fixed pH of 3. The pH of the reaction was evaluated at 1.5, 2.5, 3, 3.5, 4, 5, and 6 at a fixed 1:1 Fe:H_2O_2 molar ratio. It was not possible to perform a kinetics evaluation on the real urine, further explanations are found in the next chapter.

Evaluation of the urine concentration factor

Parameters (Molar ratio and pH) that were obtained from the previous studies on the fresh urine of Cf1 were tested on urine samples having the concentration factors Cf5 and Cf10. The reaction was carried out by adding 5 g H2O2/L, and 10 g H2O2/L, respectively at a 1:1 Fe:H_2O_2 molar ratio and a pH condition of 4.

The effect of the chemical dose

Another experiment was conducted on fresh urine Cf1 to see the effect of increasing the chemical dose Fe:H2O2/L on the COD removal, at which 1, 2, and 4 g H2O2/L were applied at a 1:1 Fe:H2O2 molar ratio and at a pH condition of 4.

The effect of high chloride ion concentration on urea compound

After measuring the urea concentrations of the previous treatments, a follow-up study was done to investigate the influence of chloride oxidation on the fate of urea during the Fenton reagent based AOP in urine.

This experiment was carried out in closed bottles of a 100 ml size containing fresh urine of Cf1 (Acidified to a pH of 4). In each bottle, a measured amount of sodium chloride NaCl was added and mixed using the magnetic stirrer. The sodium chloride was added and dissolved before applying the Fenton reagent (Fe^{2+} and H_2O_2). The increment in the chloride concentrations was calculated based on the initial concentration of the chloride ions presented in Cf1 fresh urine.

Mass balance analysis for ferrous iron Fe^{2+}

A mass balance study was carried out to evaluate the fate of iron during the AOP. The concentration of ferrous iron Fe^{2+} was measured in the treated urine samples using the Thermo Fisher Scientific Gallery Discrete Analyzer. Also, measuring the ferrous iron concentration in the precipitate (sludge) by separating the formed sludge using a funnel and a 0.45 µm filter followed by a drying step using the incubator.

After drying the filters (containing dried sludge), a measured amount of the dried sludge (g/L) was collected and dissolved in 45 mL oxalic acid at a pH affinity range between 2.5 – 3. Then measuring the ferrous iron concentration in the Thermo Fisher Scientific Gallery Discrete Analyzer. (Lee et al., 2007)

3.3 Physicochemical analysis

3.3.0 pH, urea CH_4N_2O, nitrate NO_3^-, ammonia NH_3, chloride ions Cl^-, ferrous ions Fe^{2+}, orthophosphate P, residual H_2O_2

The types of devices and test kits used in this experiment are:

1. pH measurements were done using the pH meter (CH-9100, Metrohm, Switzerland) (± 0.05) that was calibrated before every experiment using the three calibration regents of analytical grade 1.68, 4.01, and 7.
2. Urea concentration was measured in Thermo Fisher Scientific Gallery Discrete Analyzer (98610001, Thermo Fisher Scientific, Germany). Using

an enzymatic test of urease and glutamate dehydrogenase (GLDH) at 37°C using a 340 nm filter.

3. Ammonia NH_3 measurements were done in the Thermo Fisher Scientific Gallery Discrete Analyzer, in which, ammonia reacts with hypochlorite ions generated by the alkaline hydrolysis of sodium dichloroisocyanurate to form monochloramine. This reacts with salicylate ions in the presence of sodium nitroprusside at around pH 12.6 to form a blue compound. The absorbance of this compound is measured spectrophotometrically at the wavelength 660 nm and is related to the ammonia concentration by means of a calibration curve.
4. Nitrate NO_3^- concentration was measured in a colorimetric test hydrazine method in the Thermo Fisher Scientific Gallery Discrete Analyzer.
5. The total nitrogen TN was measured by first diluting the urine samples to a dilution factor of 1000-fold, 5000-fold, and 10000-fold for Cf1, Cf5, and Cf10, respectively. Then using Spectroquant Crack Set 20 (1.14963.0001, Merck KGaA, Germany) to oxidize organic and inorganic nitrogenous compounds into nitrate NO_3^- by heating the solutions inside the cells using Spectroquant Thermoreactor TR 420 (10421269, Merk KGaA, Germany) at 120°C for 60 minutes. After heating and cooling, the samples were added to 2,6-dimethylphenol (DMP) to form 4-nitro-2,6-dimethylphenol using the Spectroquant Nitrate Test (1.09713.0002) (Merck KGaA, Darmstadt, Germany) forming a coloured solution. The formed coloured solution is measured spectrophotometrically using Spectroquant NOVA 60-A Colorimeter (10460731, Merck KGaA, Germany). Total nitrogen measurements were done on both filtered (0.45 µm filter) and non-filtered urine samples.
6. Chemical oxygen demand COD was measured by Spectroquant COD Cell Test (At a range of 500-10000 mg/L) (HC17200, Merck KGaA, Germany), in which, the soluble organic compounds in the treated samples (Samples were filtered in advance using a 0.45 µm filter) are oxidized in a hot sulfuric solution of potassium dichromate, and silver sulfate catalyst. The reaction cells were then heated to 148°C for 120 minutes using the Spectroquant Thermoreactor TR 420 (10421269, Merk KGaA, Germany) forming Chromium ions Cr^{3+}. After heating and cooling Cr^{3+} ions are measured spectrophotometrically using Spectroquant NOVA 60-A

Colorimeter (10460731, Merck KGaA, Germany), which determined COD concentration (mg/L). Urine samples of the concentration factor CF5 and Cf10 were diluted to a dilution factor of 10-fold before performing the COD measurement to meet the range requirement of the test kits.

7. Chloride ions Cl^- were measured in the Thermo Fisher Scientific Gallery Discrete Analyzer, using a colorimetric method of detection with mercury (II) thiocyanate.
8. Ferrous ions Fe^{2+} were measured in the Thermo Fisher Scientific Gallery Discrete Analyzer using a colorimetric test at 37°C using a 510 nm filter and 880 nm as a side wavelength. Ferrous iron (Fe^{2+}) forms an orange-red complex with 1,10- phenanthroline.
9. Orthophosphate P ions measurements were done in the Thermo Fisher Scientific Gallery Discrete Analyzer. Orthophosphate ions react with ammonium molybdate and antimony potassium tartrate (catalyst) under acidic conditions to form a 12-molybdophosphoric acid complex. The complex is then reduced with ascorbic acid to form a blue heteropoly compound that is measured spectrophotometrically at the wavelength of 880 nm.
10. The hydrogen peroxide H_2O_2 was measured using a spectrophotometer (N4100020, PerkinElmer-Inc, USA) at a wavelength of 405 by selecting an absorbency range of 450 – 350. The measurements of the residual H_2O_2 started by creating a calibration curve of the XY-axis, where hydrogen peroxide concentration is on the X-axis and the absorbance 405-wavelength is on the Y-axis, shown in Figure (2). However, 1 mL of different concentrations of 50 % hydrogen peroxide containing 0.2 to 2.5 g/L was added to 1 mL Titanium (IV) oxysulfate – 27 – 31 % sulfuric acid hydrate reagent forming a coloured solution. Then complete the 10 mL total volume by adding 8 ml of milli-Q water and measure the absorbency at 405-wavelength to get a calibration curve. To measure the residual hydrogen peroxide concentration in the treated urine, plot the measured wavelength values from the spectrophotometer in the modelling equation found in Figure (2).

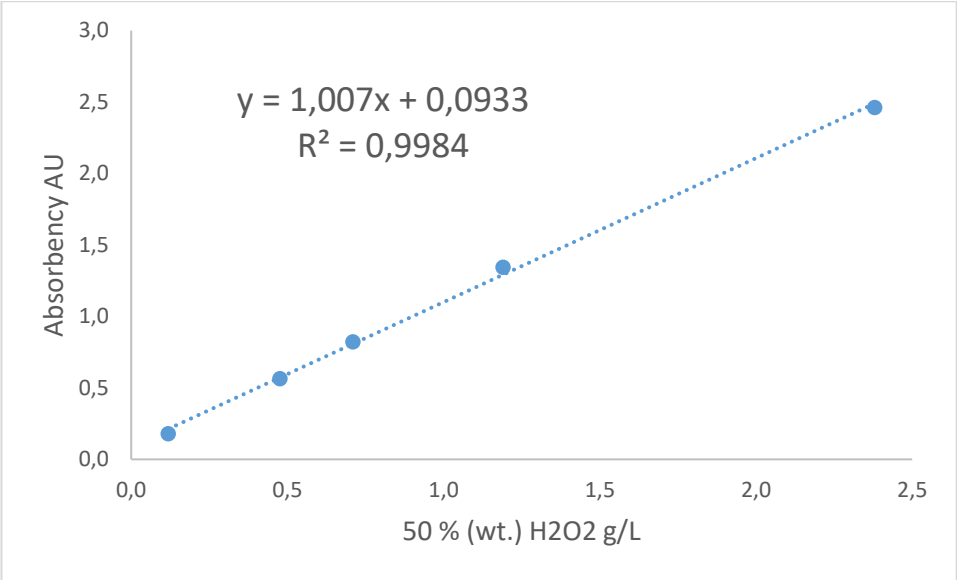


FIGURE 2. A modelling calibration curve for detecting hydrogen peroxide concentration in urine.

Curve fitting of Figure 2.

Error (Slope)	Error (Intercept)	Standard error
0.023266722	0.029107287	0.040781275

4 Results and discussion

4.1 The chemistry of Fenton Reagent-based AOP in urine

4.1.0 The effect of Fe:H2O2 molar ratio on the COD removal

Synthetic urine

The activation of hydrogen peroxide is directly proportional to the Fe:H_2O_2 molar ratio in the synthetic urine treatment. Increasing the Fe:H_2O_2 molar ratio, increased the hydrogen peroxide activation, as shown in Figure (3).

In the treatment of Cf1 synthetic urine using 1 g H_2O_2/L, a 1:5 Fe:H_2O_2 molar ratio was sufficient to allow 91% activation in the hydrogen peroxide at a fixed pH of 3. At the same parameters, a 1:10 Fe:H_2O_2 molar ratio achieved 42% activation in hydrogen peroxide.

In the Fenton oxidation treatment of the concentrated synthetic urine, 45% activation occurred in the hydrogen peroxide at a fixed pH value of 3, using 1 g H_2O_2/L at a 1:5 Fe:H_2O_2 molar ratio.

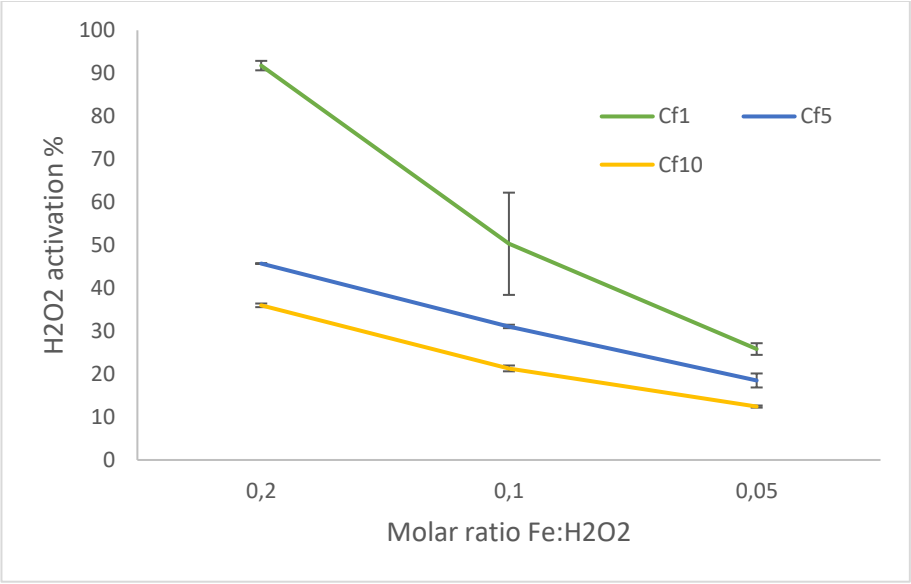


FIGURE 3. The variation of hydrogen peroxide activation as a function of Fe:H_2O_2 molar ratio in synthetic urine

The activation of hydrogen peroxide in the treatment of concentrated synthetic urine required higher concentrations of iron Fe^{2+}. The reason behind that could be related to the high ionic strength in concentrated synthetic urine, which may obstruct the hydrogen peroxide activation. (Pignatello et al., 2006)

Synthetic urine samples of the concentration factors Cf5 and Cf10 hold higher concentrations of organic carbons (Provided by the citric acid) than the synthetic urine Cf1. Organic compounds could act as scavengers to ferric iron Fe^{3+} that formed in the first reaction (equation 2). Thus, these scavengers caused a reduction in the iron catalyst and inhibited further activation in the hydrogen peroxide. (Xu et al., 2020)

Real urine

In real urine, the activation of hydrogen peroxide also occurred as a function of increasing the Fe:H2O2 molar ratio, as shown in Figure (4). In the treatment of Cf1 urine, it required a 1:1 Fe:H_2O_2 molar ratio to fully activate the hydrogen peroxide at a pH condition of 3. Furthermore, COD removal did not change at a 1.5:1 Fe:H_2O_2 molar ratio, thus the 1:1 Fe:H_2O_2 molar ratio was enough to activate all hydrogen peroxide. Also, shown in Figure (4), a 33.6% removal in COD occurred at a 1:1 Fe:H_2O_2 mole ratio, while the 1:2 Fe:H2O2 mole ratio reached 14.4% removal in COD.

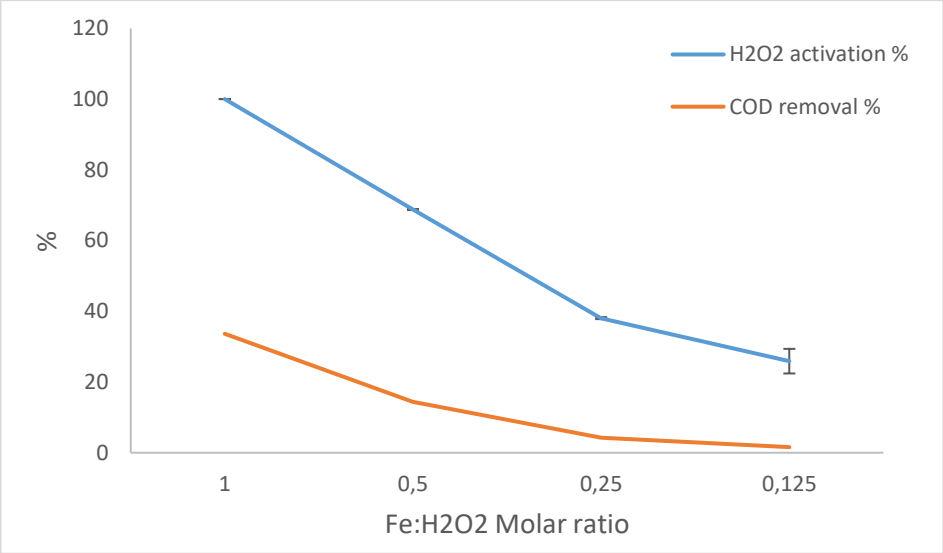


FIGURE 4. The variation of the hydrogen peroxide activation as a function of Fe:H2O2 Molar ratio in real urine (Cf1) at pH 3.

The results state, that in real urine, it was essential to add more of the ferrous iron Fe^{2+} to activate the hydrogen peroxide than in the case of the synthetic urine. The difference between both urine solutions (real and synthetic) is the concentration of organic complexes present in real urine, as shown in Table (1).

One of the reasons behind the high demand for ferrous iron could be that the organic compounds present in real urine are scavenging some of the ferric iron Fe^{+3} that is formed in equation (2) through a ligand exchange mechanism. (Ma et al., 2022) As a result, forming a precipitate of organic compounds containing Fe^{3+}. Thus, the reduction in ferric iron led to a reduction in the ferrous iron (catalyst), eventually interrupting the cycle of the Fenton oxidation process.

4.1.1 The effect of pH condition on the COD removal

Regarding the results that are obtained from the study effect of pH condition on the activation of the hydrogen peroxide in both real urine and synthetic urine.

Synthetic urine

In the treatments of all the synthetic urine solutions (Cf1, Cf5, and Cf10), it was observed, that a pH value between 2.5 - 3 was an effective condition to activate the hydrogen peroxide compared to a pH of 3.5, using 1 g H_2O_2/L at a fixed 1:5 Fe:H_2O_2 molar ratio, as shown in Figure (5).

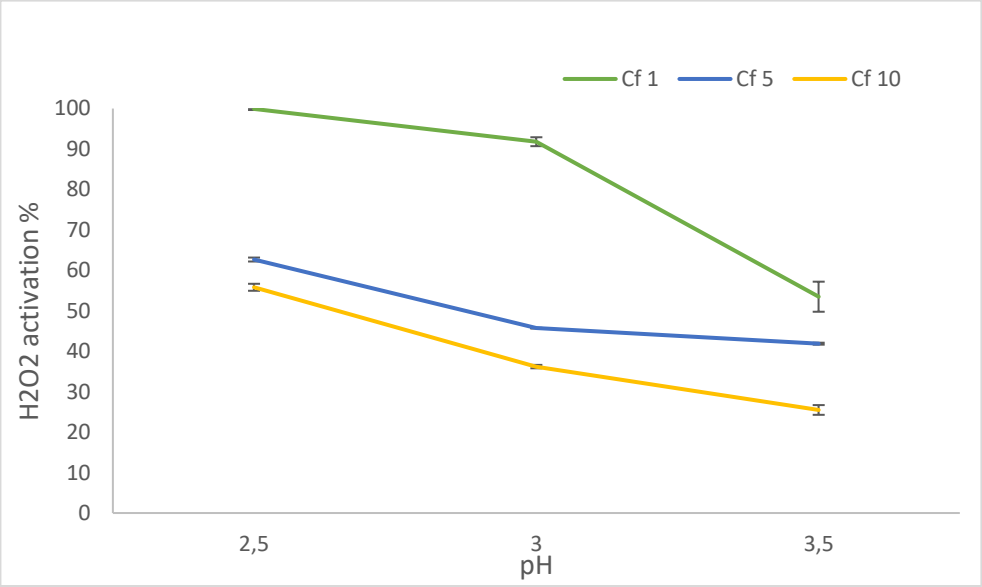


FIGURE 5. Shows the effect of pH on the activation of hydrogen peroxide during the Fenton Oxidation treatment of the synthetic urine at a 1:5 Fe:H_2O_2 molar ratio.

The theory behind the activation of the hydrogen peroxide in this case is related to the iron speciation in an aqueous solution, at a pH range of 2.5 - 3 found both iron Fe^{2+} and Fe^{3+}. While at a pH of 3.5 initiated low fractions of Fe^{2+} and Fe^{3+}, which are essential in the Fenton reagent AOP occurrence. (Furcas et al., 2021, Pignatello et al., 2006)

Real urine

In Cf1 fresh urine treatment occurred full activation in hydrogen peroxide at the pH range 1.5 - 6, using 1 g H_2O_2/L at a fixed 1:1 Fe:H_2O_2 molar ratio. However, the highest COD removal is 39%, which occurred at pH 4, as shown in Figure (6).

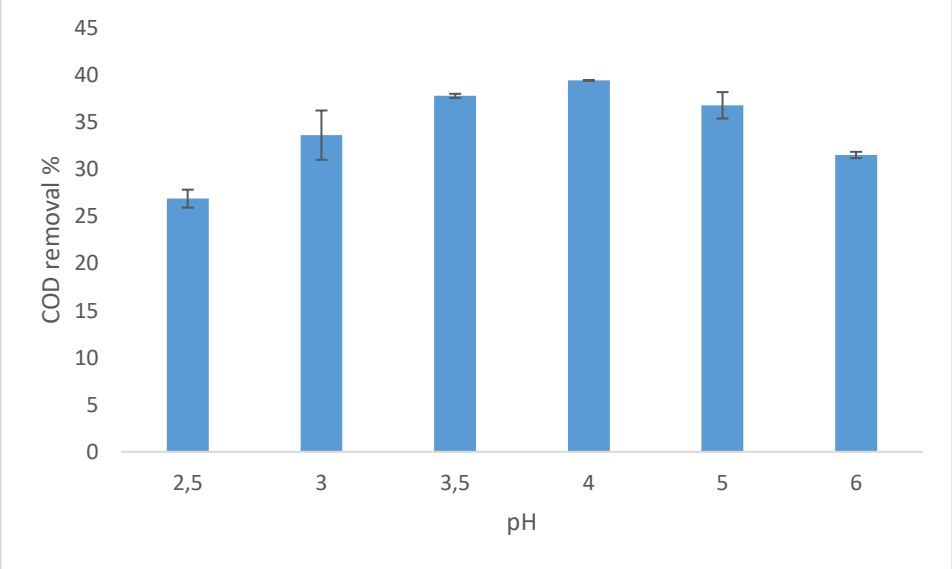


FIGURE 6. Illustrate the COD removal at different pH conditions for fresh urine Cf1 treated with 1 g H_2O_2/L at a 1:1 Fe:H_2O_2 molar ratio.

The Fenton reagent AOP cycle (equations 2 and 3) is expected to occur at the pH range between 2.5–3, which involves the formation of ferric ions Fe^{3+} and the regeneration of the ferrous ions Fe^{2+}. (Xu et al., 2020)

The difference in COD removal in the studied pH conditions is not significantly high. However, observed less removal in COD concentration at the pH range of 2.5-3 compared to other pH conditions, suggesting that a portion of the reaction might have followed a non-radical pathway.

To support this hypothesis: a previous study was conducted on the evolution of oxygen gas during Fenton oxidation at a pH range between 1 – 2.54. (Kremer, 2003) The result revealed an increase in the formation rate of oxygen gas when pH was increased to a value of 2.54. The mechanism of this reaction involved the formation of the Ferryl-oxo-complex (FeO^{2+}). Ferryl-oxo-complex is an active intermediate that follows several reaction pathways, which lead to the degradation process of the hydrogen peroxide, forming water and oxygen gas O_2. (Kremer, 2003, Arsene, Gorinchioy, 2019)

The reaction pathways of the Ferryl-oxo-complex in the Fenton oxidation process happen as follows: It reacts with another hydrogen peroxide molecule, forming the ferrous ion Fe^{2+} and an oxygen molecule. It also reacts with Fe^{2+} to form Fe^{3+}. Lastly, the reaction with ferric ion Fe^{3+}, forms binuclear complex $(FeOFe)^{5+}$, which undergoes further reaction with hydrogen peroxide forming O_2. (Kremer, 2003, Arsene, Gorinchioy, 2019)

On the other hand, at a pH range between 3.5 - 6, ferrous iron Fe^{2+} is found in another form of iron hydroxide $Fe(OH)_2$ that is 10 times more reactive. (Pignatello et al., 2006) Thus, iron hydroxide $Fe(OH)_2$ is the catalyst form of iron in this pH range. At this pH range, the reaction of hydrogen peroxide and iron hydroxide allowed a higher formation of hydroxyl radicals compared with ferrous iron Fe^{2+}, resulting in higher COD removal. Also, the result of this reaction led to the formation of ferric oxide species that instantly precipitated during the treatment. This means, that the second reaction (equation 3) of the Fenton oxidation cycle did not occur in such pH range (I.e., 3.5 - 6). The lower COD removal at pH 6 can be attributed to the lower oxidation potential of the hydroxyl radical. (Saharan et al., 2014)

Ferrous iron concentrations in the treated urine samples from the pH study were tested. The results showed that ferrous iron is found at pH conditions in the range of 2.5 - 3.5, as shown in Figure (7). Whereas at pH conditions above 3.5, noticed less concentration of ferrous iron because it is dissociated in the form of iron hydroxide $Fe(OH)_2$, which has precipitated in the sludge.

The result from this analysis proves that the Fenton reagent cycle cannot be occurred at pH conditions ≥3.5 because the catalytic form of iron (I.e., ferrous iron) is found to have low fractions in such pH conditions.

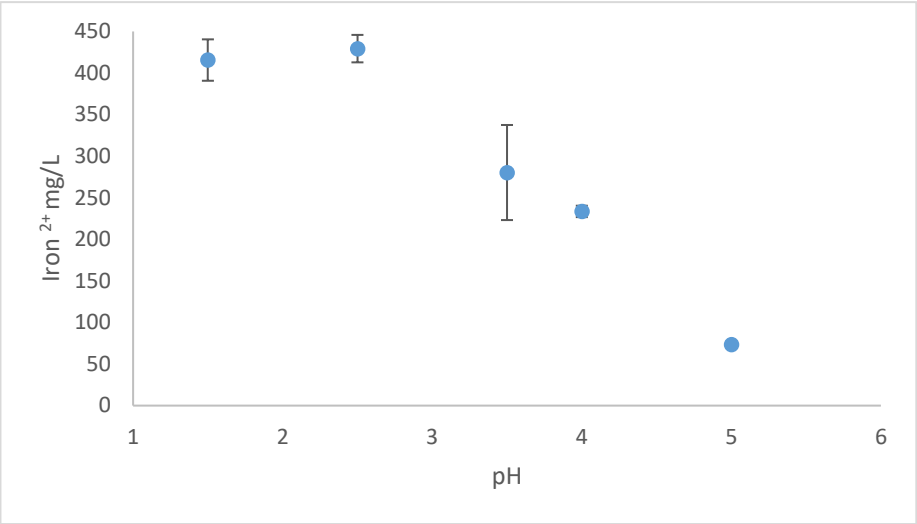


FIGURE 7. Shows iron Fe^{2+} residual in Cf1 fresh urine treated with 1 g H_2O_2/L at a 1:1 Fe:H_2O_2 molar ratio in acidic conditions.

During the experiment of the pH study, occurred less formation of sludge at a pH range between 2.5 - 3, which means that the formed ferric ions Fe^{3+} in the first reaction are reduced to ferrous ions Fe^{2+} in the second reaction (No iron precipitation occurs). On the other hand, at a pH range between 3.5 – 6, higher formations of sludge occurred in the bottom of the reaction beakers. This means, that the iron hydroxide $Fe(OH)_2$ compounds are oxidized in the first reaction forming ferric iron species, which hydrolyses and then precipitate in the form of ferric oxyhydroxides.

The colour of the treated urine and the sludge appeared differently in the experiment of each pH condition. At the pH range of 2.5 - 5, the colour of the treated urine ranged from light green to dark green, while the colour of the sludge graduated from light grey to dark grey as the pH increased. At the pH conditions of 1.5, and 6, formed less sludge than the other pH conditions, and both the treated urine and the formed sludge appeared brown in colour.

4.1.2 Kinetic evaluation

Synthetic urine

The kinetic study of the Fenton reagent based AOP was conducted on synthetic urine at a pH condition of 3 and a 1:5 Fe:H_2O_2 molar ratio. The results showed, almost full activation of hydrogen peroxide in Cf1 synthetic urine within 2 hours of reaction time, at the same time occurred about half activation in the hydrogen peroxide in the treatment of synthetic urine Cf5 and Cf10, as shown in Figure (8).

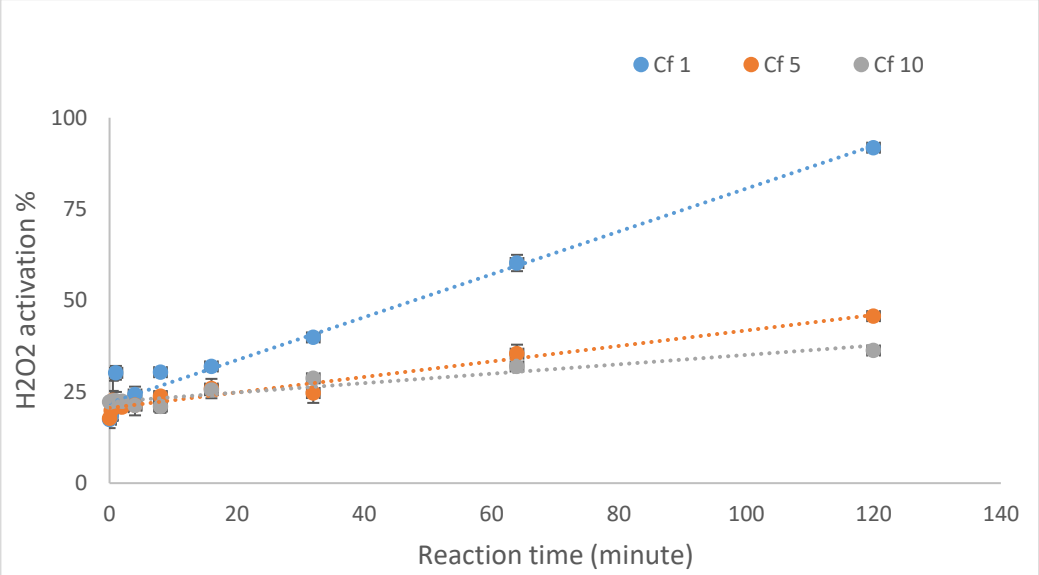


FIGURE 8. Shows the kinetic study of the Fenton reagent AOP in Cf1, Cf5, and Cf10 synthetic urine at pH 3 and 1:5 Fe:H_2O_2 molar ratio.

In this case, the Fenton oxidation cycle occurred, at which the small fraction of the ferrous iron Fe^{2+} was regenerated in the second reaction (equation 3) at a pH value of 3, allowing the activation of hydrogen peroxide to happen slowly in a cycle.

The residual hydrogen peroxide concentration was measured for synthetic urine samples of Cf5 and Cf10 after 24 hours of mixing. The results showed no change in H_2O_2 concentration. In this case, occurred the reaction between the organic compounds and the ferric iron formed a precipitate. Eventually, it reduced the iron catalyst, inhibiting further activation in the hydrogen peroxide.

Real urine

In real urine, the activation of the hydrogen peroxide occurred within 5 minutes. Here, the activation of the hydrogen peroxide occurred by another form of iron hydroxide $Fe(OH)_2$ which is 10 times more reactive than the ferrous iron Fe^{2+}. Thus, $Fe(OH)_2$ ionic compounds are oxidized in the first reaction of the Fenton oxidation forming ferric iron species that tend to precipitate instantly in such parameters (I.e., 1:1 $Fe:H_2O_2$ and pH 4). Thus, this quick precipitation did not allow the Author to perform the kinetic study.

4.2 The fate of phosphorous in real urine after the Fenton reagent based AOP

The orthophosphate analysis was done on the treated real urine samples from the pH study, as shown in Figure (9). At the pH range of 2.5 - 6, no phosphorous ions were detected in the treated urine samples, which gives the only possible explanation, that the phosphorous ions were precipitated in the sludge during the treatment in the form of iron (III) phosphate $FePO_4$ or iron (II) phosphate (vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$).

This is delegated to the fact that the second reaction (equation 3) of reducing the ferric ions to ferrous ions is slower than the first reaction (equation 2), which allows the scavenging of the ferric ions by the phosphorus ions forming iron phosphate precipitate. (Pignatello et al., 2006)

Also, this finding provides another reason behind the high demand for the iron catalyst (Ferrous iron Fe^{2+}).

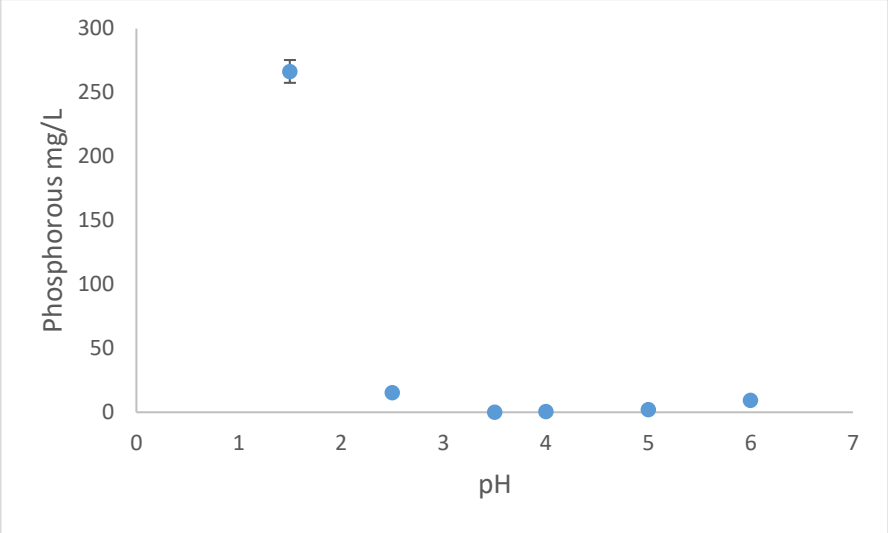


FIGURE 9. Shows the residual phosphorous concentrations in fresh urine samples after Fenton oxidation treatment using 1 g H_2O_2/L at a 1:1 Fe:H_2O_2 molar ratio.

Iron phosphate precipitate can be recovered in many techniques (e.g., acid extraction process). (Pereira & Papini, 2015) It requires further research to determine the most feasible process that could give the highest recovery in phosphorus.

4.3 Nitrogen loss in real urine after the Fenton reagent based AOP

Urea loss was observed after the Fenton oxidation treatment of all the real urine samples. This led to further analysis and research to find out the cause behind the nitrogen loss. It was discovered that a loss occurred in the chloride ions as well, which was identical to the loss in urea, as shown in Figure (10).

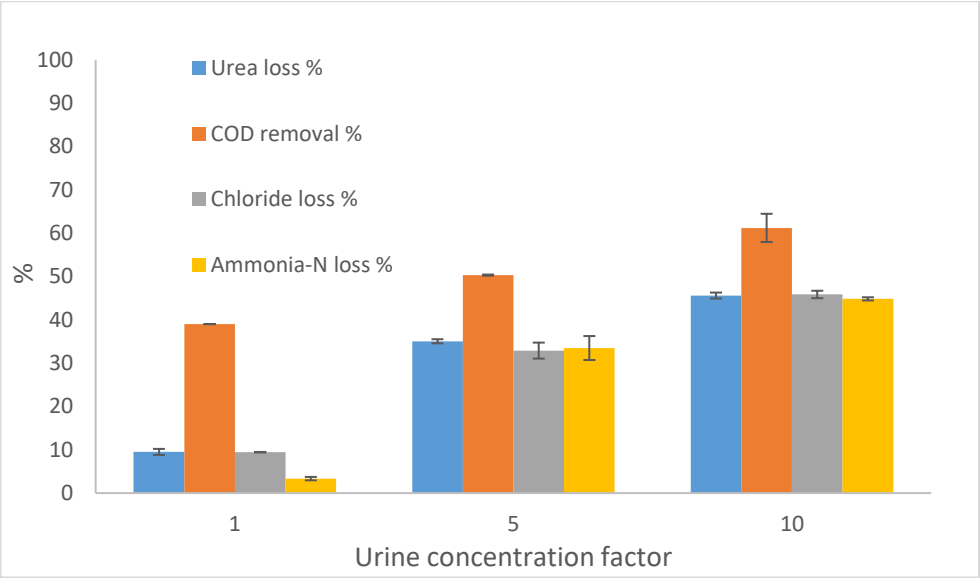


FIGURE 10. Shows the fate of organic and inorganic compounds after the Fenton oxidation of real urine treated with 1, 5, and 10 g H_2O_2/L for Cf1, Cf5, Cf10, respectively at a 1:1 Fe:H_2O_2 molar ratio and pH 4.

A follow-up study was then conducted on the loss of urea in the presence of chloride ions, in which different chloride concentrations were dissolved into Cf1 urine before the Fenton oxidation treatment. It was found that high chloride concentrations increase urea loss, as shown in Figure (11).

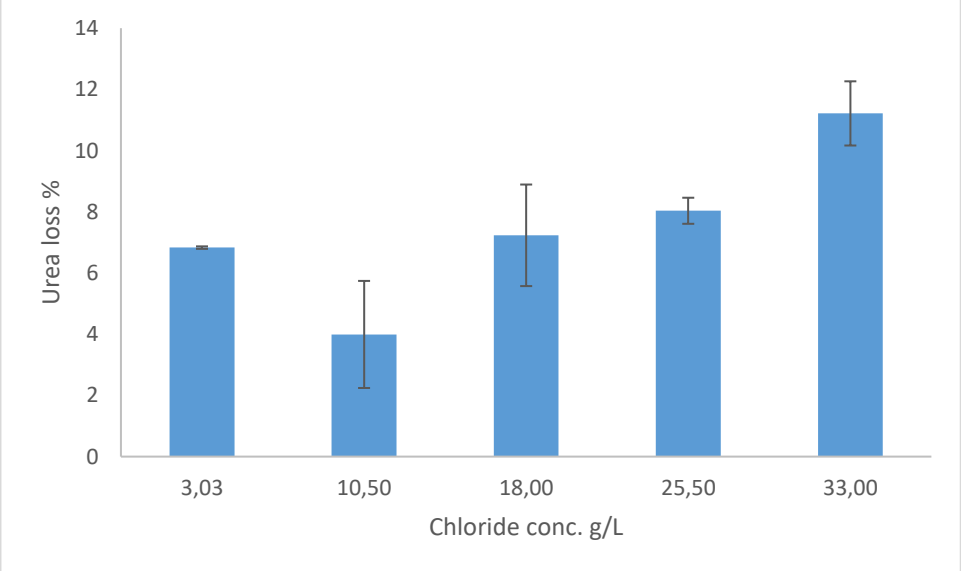


FIGURE 11. Shows urea loss in the presence of chloride concentrations after the Fenton AOP on fresh urine Cf1 at a 0.86:1 Fe:H_2O_2 molar ratio and a pH of 4.

To explain the loss in urea, we must understand the chemical reaction between the hydroxy radical •OH and the inorganic compounds found in urine. As mentioned earlier, the presence of halide compounds (Cl^- and Br^-) interferes with the hydroxyl radical •OH. A study was conducted on the degradation of pharmaceuticals in human urine using electrochemical AOP. (Clark et al., 2021) Revealed, an anodic oxidation occurs between the hydroxyl radicals and the free chlorine ions presenting in urine forming hypochlorous acid ($HOCl^-$), that dissociates to form hypochlorite ions (OCl^-) and free hydrogen ions. The oxidation continues to the formation of chloride Cl• and dichloride Cl_2• radicals with standard redox potential E° equal to 2.34 and 2.13, respectively.

However, the standard redox potential of the hydroxyl radical is higher, but Cl• and Cl_2• radicals are more attractive to oxidize nitrogen compounds. (Clark et al., 2021) Thus, the formation of halide radicals led to rapid degradation in the urea or NH_4^+/NH_3, forming intermediates of organic and inorganic chloramines (NH_2Cl, $NHCl_2$, and NCl_3).

In the presence of low concentrations of urea, the subsequent oxidation of the free chloride ions by the hydroxyl radicals favourites another reaction pathway forming oxychloride intermediates (chlorate ClO3 and perchlorate ClO_4^-). The inhibition of oxychloride formation occurs by increasing urea concentration. (Clark et al., 2021)

Another study was done by Zhaoxi, S., Jinhua, L., et al on the oxidation of organic carbon in urine using the photoelectrochemical method. The study stated serial reactions between the hydroxyl radicals and the chloride ions. The end-product of these reactions is nitrogen gas N_2, as shown in equations (10, 11, 12, 13, 14, 15, 16, and 17). (Shen et al., 2019)

$$NH_2CONH_2 + 2\mathrm{Cl}\bullet + \mathrm{H_2O} \rightarrow 2NH_2\bullet + CO_2 + 2Cl^- + 2\mathrm{H}^+ \quad (10)$$

$$NH_2\bullet + \mathrm{HOCl} \rightarrow NH_2\mathrm{Cl} + \mathrm{OH}\bullet \quad (11)$$

$$NH_2\mathrm{Cl} + \mathrm{Cl}\bullet \rightarrow \mathrm{NHCl}\bullet + \mathrm{Cl}^- + \mathrm{H}^+ \quad (12)$$

$$\mathrm{NHCl}\bullet + \mathrm{HOCl} \rightarrow \mathrm{NHCl_2} + OH\bullet \quad (13)$$

$$NHCl_2 + H_2\mathrm{O} \rightarrow \mathrm{NOH} + 2H^+ + 2Cl^- \quad (14)$$

$$NHCl_2 + \mathrm{NOH} \rightarrow \mathrm{N_2} + \mathrm{HCl}O + H^+ + Cl^- \quad (15)$$

$$NH_2\bullet + OH\bullet \rightarrow NH_2OH \quad (16)$$

$$NH_2OH + OH\bullet \rightarrow NO_2^- \rightarrow NO_3^- \quad (17)$$

After analysing the nitrate concentration mg/L in the treated samples, found that NO_3^- concentration didn't change after the Fenton oxidation treatment, meaning that the last reaction in equation (17) did not occur in this study.

The results in Figure (10) showed that in the treatment of high concentration factors urine resulted in a higher loss in urea, ammonia-Nitrogen, and chloride at 1:1 Fe:H_2O_2 molar ratio and 4 pH condition. The hypothesis behind the loss in urea and ammonia-N is the high concentration of chloride ions found in Cf10 than in Cf1 urine, leading to a higher loss in urea, and ammonia-N. Whereas the higher loss in chloride concentration in the Fenton oxidation treatment of Cf10 urine is linked to the higher chemical dose of the oxidant hydrogen peroxide added in the treatment of the Cf10 (5 g H_2O_2/L) urine than in Cf1 (1 g H_2O_2/L) urine.

Total nitrogen TN measurement was done on filtered and non-filtered urine samples after the Fenton oxidation treatment, as shown in Figure (12). The objective was to check if the loss of nitrogen compounds accumulated in the sludge.

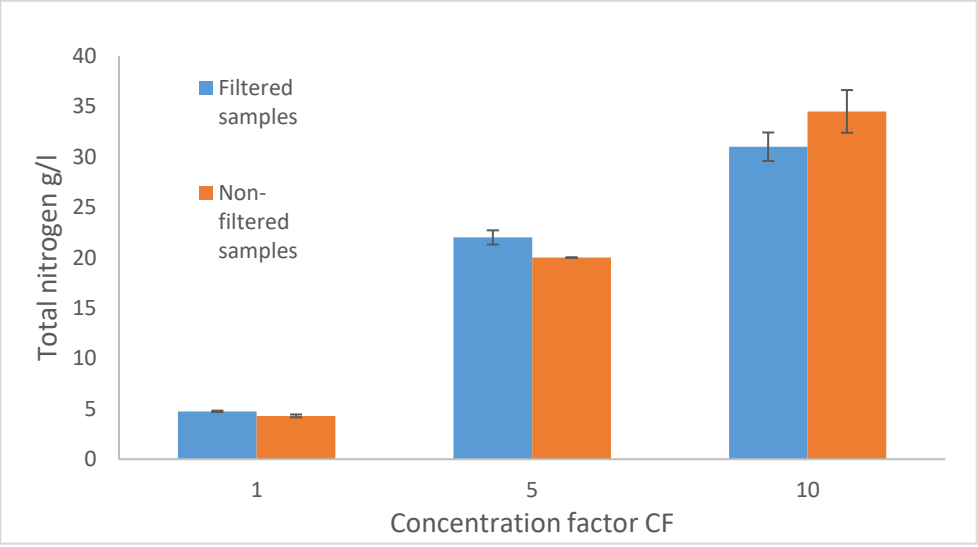


FIGURE 12. Shows the concentration of total nitrogen in urine samples having different concentration factors after the Fenton oxidation process of using 1 g H_2O_2/L at a 0.86:1 Fe:H2O2 and a pH of 4.

The results revealed that the total nitrogen in both samples is almost identical, accounting for the dilution and analytical error of the spectrophotometer used in the experiment. Further investigation needs to be done to prove this hypothesis. However, this finding gives further support to the hypothesis, that urea loss occurred during the oxidation in the form of nitrogen gas N_2.

It is believed in this research, that if chloride ions are extracted from the urine before the Fenton oxidation process, most of the nitrogen compounds (e.g., urea) will be preserved in the final product.
The process of chloride ions extraction can be done by using a resin (Ion exchange), which leads to further research to determine the most applicable resin for this process.

4.3.0 Mass balance analysis on the total Nitrogen in real urine

This section provides a mass balance analysis for the total nitrogen before and after the Fenton reagent based AOP. As shown in Diagram 1, low losses in the total nitrogen after the Fenton oxidation process of the fresh urine Cf1 occur in comparison to the concentrated urine (I.e., Cf5, and Cf10 urine).

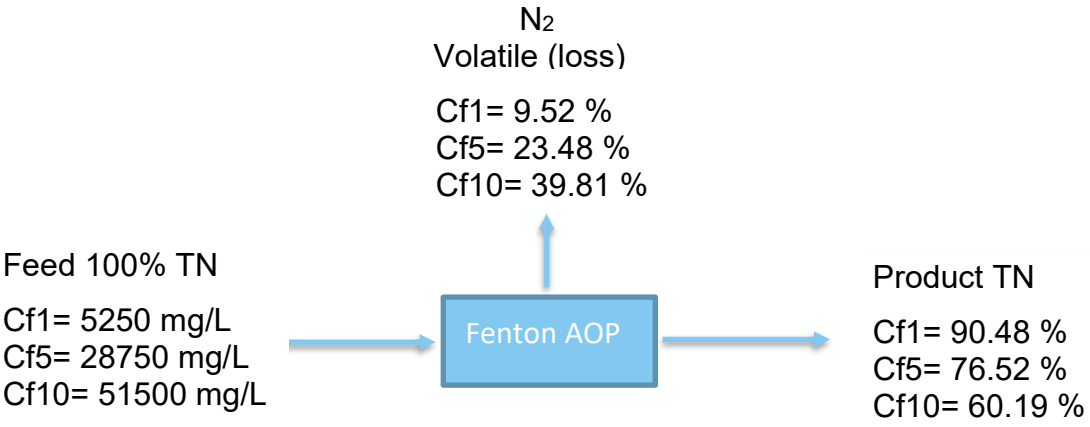


DIAGRAM 1. Shows the mass balance of the total nitrogen concentration flows in the treatments of real urine at different concentration factors (Cf1, Cf5, and Cf10) using 1 g H_2O_2/L, at 0.86:1 Fe:H_2O_2 molar ratio and pH of 4.

4.4 The effect of the chemical dose on organic and inorganic compounds in real urine after the Fenton reagent based AOP

This study was performed in fresh urine Cf1 at a 1:1 Fe:H_2O_2 molar ratio and pH value of 4. The results state that increases in the chemical dose of the reagent (Fe^{2+} and H_2O_2) resulted in higher losses in urea, ammonia-Nitrogen, and chloride while reaching higher removal in the COD content (80%), Figure (13).

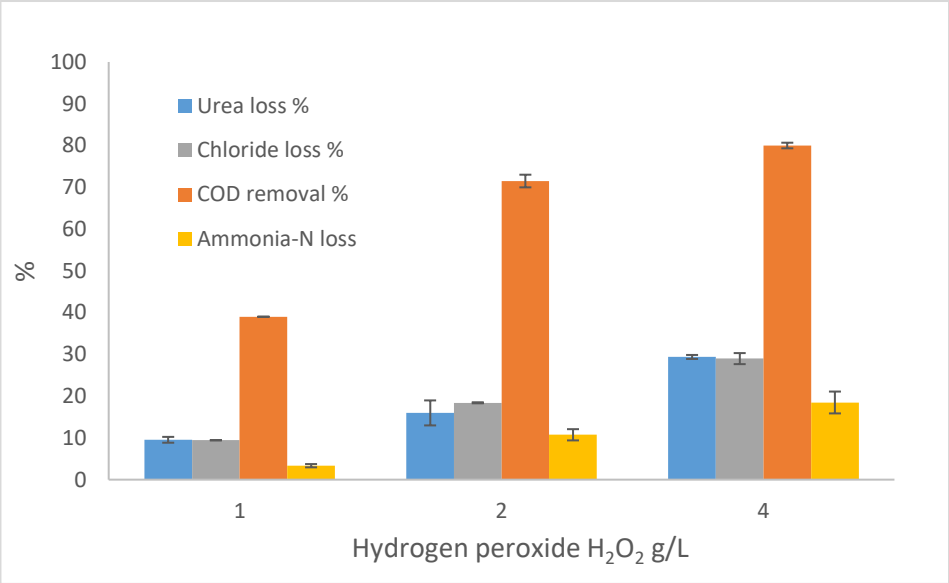


FIGURE 13. Shows the fate of organic and inorganic compounds after the Fenton oxidation in fresh urine Cf1 at higher chemical doses of a 1:1 Fe:H_2O_2 molar ratio and a pH of 4.

Increasing the chemical dose of the hydrogen peroxide and the iron catalyst Fe^{2+} increases the hydroxyl radical formation •OH. Thus, the higher formation in the hydroxyl radical •OH led to higher oxidation of the organic and inorganic compounds in urine.

4.5 Mass balance analysis on the iron content in real urine

A mass balance study was performed to determine the pathways of the ferrous iron in the system as well as to determine the most optimal Fe:H_2O_2 molar ratio. In real urine, was detected a negligible concentration of ferrous iron Fe^{2+} before

the Fenton oxidation treatment. The residual ferrous iron Fe^{2+} in urine was measured after the treatment using a 1:1 $Fe:H_2O_2$ molar ratio and a pH of 4.

It was found that some of the ferrous ions Fe^{2+} accumulated in the treated urine. This led to further calculations to determine the right dose of the initial amount of ferrous iron solution. It was found at a 0.86:1 $Fe:H_2O_2$ molar ratio, most of the iron has been consumed during the treatment and eventually accumulated in the sludge in the two forms of iron Fe^2 and Fe^{3+}, as shown in Diagram (2).

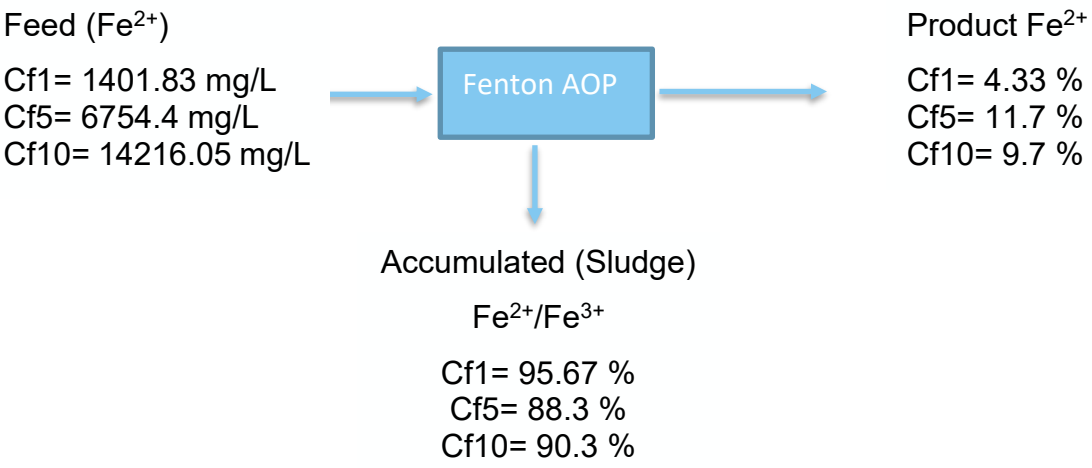


DIAGRAM 2. Shows the mass balance of the ferrous Fe^{2+} concentration flows in the treatments of the real urine at 0.86:1 $Fe:H_2O_2$ molar ratio and pH of 4.

Ferrous ions Fe^{2+} were detected in the sludge of fresh urine Cf1 treated with a 1 g H_2O_2/L at 0.86:1 $Fe:H_2O_2$ molar ratio in a pH condition of 4.

However, 4.33 % of the initial ferrous iron remained in the treated samples, and 95.67 % was accumulated in the sludge in the form of Fe^2 (9.38 %), and Fe^{3+} (86.29 %).

After correcting the mass balance found that the optimal $Fe:H_2O_2$ molar ratio in the Fenton oxidation treatment of Cf1 real urine is between 0.80:1 – 0.85:1. Whereas the optimal $Fe:H_2O_2$ molar ratio in the treatment of Cf5 and Cf10 real urine is in the range 0.70:1 – 0.75:1, depending on the COD and phosphorus concentrations of the treated urine.

The formed sludge (precipitate) during the Fenton oxidation process can be treated to recover the ferrous ions Fe^{2+}, which can be used again in the process to activate the hydrogen peroxide. This treatment is done in two stages; First, the

sludge is treated biologically by iron-reducing bacteria under anaerobic conditions, where residual organic matter found in the sludge serves as electron donor specie to reduce Fe^{3+} to Fe^{2+}.

The second stage involves an acidification process at a pH condition of 3.5, where the formed intermediate sludge is acidified by a strong acid (e.g., 1M HCl) to extract Fe^{2+} ions. The remaining sludge from the acidification process is recycled back to the digestion tank (zero waste generation). As a result, 90% of the added iron Fe^{2+} was restored, which led to a reduction in the process cost by 60%. (Shi et al., 2022)

Iron sludge may hold toxic compounds, it must undergo further treatment to ensure safe utilization and prevent it from reaching the environment. Thus, a follow-up study will be conducted on the sludge treatment after the Fenton oxidation process of organic/inorganic compounds in urine.

5 Conclusion

- The Fenton reagent based AOP occurred differently in real urine than in synthetic urine.
- The optimal Fe:H_2O_2 molar ratio is 0.80:1–0.85:1 for Cf1 fresh urine, and 0.70:1–0.75:1 for Cf5 and Cf10 urine, with respect to the increase in hydrogen peroxide dose g/L in urine treatments of Cf5 and Cf10.
- When increasing the hydrogen peroxide dose, a lower Fe:H_2O_2 molar ratio is required to achieve a full activation in the hydrogen peroxide.
- The Fenton oxidation process of organic compounds in urine was best at a pH condition of 4.
- The Fenton reagent based AOP is less active in pH conditions near neutral values as well as in very acidic conditions (e.g., pH <2.5).
- The Fenton reagent based AOP cycle didn't occur at pH 4 due to the precipitation of the iron catalyst at a pH value >3.5.
- The activation of the hydrogen peroxide happened by the other form of ferrous iron, iron hydroxide $Fe(OH)_2$.
- The high demand for iron catalysts in this study is delegated to the high concentrations of COD and phosphorus in the urine.
- Nitrogen loss was caused by the oxidative reaction with the chloride •Cl and chlorine •Cl2 radicals, N_2 nitrogen gas is the end-product of this oxidation.
- Phosphorus loss was caused by the chemical reaction between the phosphorus ions and ferric/ferrous ions forming a precipitate of iron (III) phosphate or iron (II) phosphate.

5.1 Practical Implications of this Thesis

- This research provides constructive explanations on the chemistry behind Fenton’s reagent-based advanced oxidation process in real and synthetic urine.
- Also, it shows the optimal parameters i.e., Fe:H_2O_2 molar ratio and pH condition of the Fenton reagent that achieve high removal of organic compounds in urine.

- The Fenton's reagent parameters in this study can be used to remove a selective number of COD from urine as well as treat influent wastewater with a high COD content of (5000 - 60000) mg/L.
- This paper provides a model equation, which can be used to measure hydrogen peroxide concentration in an aqueous solution at a range of (0.2 - 2.5) g H_2O_2/L.
- The Fenton oxidation process of organic compounds in urine occurred in the first five minutes of the reaction at ambient conditions (22°C and 1 atm) thus, it is considered a quick and feasible treatment.
- Regarding nitrogen loss, it is more applicable to treat fresh urine of Cf1 than concentrated urine.
- To minimize sludge formation during the treatment of wastewaters with similar characteristics to urine, this study suggests conducting the Fenton oxidation process at a pH range of 2.5-3
- This method can be applied to treat urine to produce hygienic and safe fertilizer with a high nutrient capacity. Also, the implication of this study will preserve the nutrients cycle.
- The treated urine can be dried in a substrate mixture (e.g., wheat barn and biochar mixture) to produce solid fertilizer. (Simha et al., 2020)

5.1.0 Future research

- Sludge treatment to recover ferrous iron Fe^{2+} and reuse in the process as well as to make safe use of the remaining sludge.
- The elimination of chloride ions from urine before the Fenton oxidation process prevents nitrogen loss.
- The extraction of phosphorous ions from urine as a pre-treatment to the Fenton oxidation process reduces the chemical dose of the iron catalyst Fe^{2+} that is required in the treatment.
- Or recovery of phosphorus from the sludge.

Acknowledgments

This study was done at the Swedish University of Agricultural Sciences SLU. Special thanks to my supervisor Prithvi Simha, who helped me to analyse the results of this research. This research is new thus, it will be followed by further studies to complete the whole process of urine treatment to produce a hygienically safe fertilizer in a solid form. Stay updated because science is unlimited.

REFERENCES

Arsene, I., Gorinchioy, N. (2019). *DFT STUDY OF THE ENTIRE REACTION CYCLE OF H2O2 DECOMPOSITION AND O2 GENERATION CATALYZED BY FENTON REAGENT*. http://cjm.ichem.md/dft-study-of-the-entire-reaction-cycle-of-h2o2-decomposition-and-o2-generation-catalyzed-by-fenton-reagent

Advancements in the Fenton Process for Wastewater Treatment | IntechOpen. (n.d.). Retrieved May 30, 2023, from https://www.intechopen.com/chapters/70242

Branch, L. S. (2021, May 1). *Consolidated federal laws of Canada, Canadian Environmental Protection Act, 1999*. https://laws-lois.justice.gc.ca/eng/acts/c-15.31/

Clark, J. A., Yang, Y., Ramos, N. C., Hillhouse, H. W. (2021). Selective oxidation of pharmaceuticals and suppression of perchlorate formation during electrolysis of fresh human urine. *Water Research*, *198*, 117106. https://doi.org/10.1016/j.watres.2021.117106

Courtney, C., Randall, D. G. (2022). A hybrid nanofiltration and reverse osmosis process for urine treatment: Effect on urea recovery and purity. *Water Research*, *222*, 118851. https://doi.org/10.1016/j.watres.2022.118851

Dorfman, L.M., Adams, G.E. (1973). Reactivity of the Hydroxyl Radical in Aqueous Solutions.

Furcas, F., Lothenbach, B., Isgor, O., Mundra, S., Zhang, Z., Angst, U. (2021). Solubility and speciation of iron in cementitious systems. *Cement and Concrete Research*, *151*, 106620. https://doi.org/10.1016/j.cemconres.2021.106620

Frontiers | Alkaline Dehydration of Human Urine Collected in Source-Separated Sanitation Systems Using Magnesium Oxide. (n.d.). Retrieved May 30, 2023, from https://www.frontiersin.org/articles/10.3389/fenvs.2020.619901/full?utm_source=dlvr.it&utm_medium=twitter

Fenton and Fenton-like wet oxidation for degradation and destruction of organic radioactive wastes | npj Materials Degradation. (n.d.). Retrieved May 30, 2023, from https://www.nature.com/articles/s41529-021-00192-3

Hydrogen Peroxide. (n.d.). Retrieved May 30, 2023, from https://www.lenntech.com/library/oxidation/h2o2/hydrogen-peroxide.htm

Haber-Bosch Process. (n.d.). Retrieved May 30, 2023, from http://large.stanford.edu/courses/2022/ph240/jimenez2/

Köpping, I., McArdell, C. S., Borowska, E., Böhler, M. A., Udert, K. M. (2020). Removal of pharmaceuticals from nitrified urine by adsorption on granular activated carbon. *Water Research X*, *9*, 100057. https://doi.org/10.1016/j.wroa.2020.100057

Jiaying, M., Tingting, C., Jie, L., Weimeng, F., Baohua, F., Guangyan, L., Hubo, L., Juncai, L., Zhihai, W., Longxing, T., & Guanfu, F. (2022). Functions of Nitrogen, Phosphorus and Potassium in Energy Status and Their Influences on Rice Growth and Development. *Rice Science*, *29*(2), 166–178. https://doi.org/10.1016/j.rsci.2022.01.005

Kremer, M. L. (2003). The Fenton Reaction. Dependence of the Rate on pH. The Journal of Physical Chemistry A, 107(11), 1734–1741. https://doi.org/10.1021/jp020654p

López-Maldonado, E. A., Oropeza-Guzman, M. T., Jurado-Baizaval, J. L., Ochoa-Terán, A. (2014). Coagulation–flocculation mechanisms in wastewater treatment plants through zeta potential measurements. *Journal of Hazardous Materials*, *279*, 1–10. https://doi.org/10.1016/j.jhazmat.2014.06.025

Li, X., Wang, B., Liu, F., Yu, G. (2023). Occurrence and Removal of Pharmaceutical Contaminants in Urine: A Review. *Water*, *15*(8), Article 8. https://doi.org/10.3390/w15081517

Lee, H., Shoda, M. (2008). Removal of COD and color from livestock wastewater by the Fenton method. *Journal of Hazardous Materials*, *153*(3), 1314–1319. https://doi.org/10.1016/j.jhazmat.2007.09.097

Lee, S. O., Tran, T., Jung, B. H., Kim, S. J., Kim, M. J. (2007). Dissolution of iron oxide using oxalic acid. *Hydrometallurgy*, *87*(3), 91–99. https://doi.org/10.1016/j.hydromet.2007.02.005

Ling, J., de Toledo, R. A., Shim, H. (2016). Chapter 8—Biodiesel Production From Wastewater Using Oleaginous Yeast and Microalgae. In M. N. V. Prasad & K. Shih (Eds.), *Environmental Materials and Waste* (pp. 179–212). Academic Press. https://doi.org/10.1016/B978-0-12-803837-6.00008-1

Membrane technologies in toilet urine treatment for toilet urine resource utilization: A review—RSC Advances (RSC Publishing) DOI:10.1039/D1RA05816A. (n.d.). Retrieved May 30, 2023, from https://pubs.rsc.org/en/content/articlehtml/2021/ra/d1ra05816a

Ma, W.-W., Zhu, M.-X., Yang, G.-P., Li, T., Li, Q.-Q., Liu, S.-H., Li, J.-L. (2022). Stability and molecular fractionation of ferrihydrite-bound organic carbon during iron reduction by dissolved sulfide. *Chemical Geology*, *594*, 120774. https://doi.org/10.1016/j.chemgeo.2022.120774

Ozone used for COD Reduction in Wastewater – Oxidation Technologies News. (n.d.). Retrieved May 30, 2023, from https://www.oxidationtech.com/blog/ozone-used-for-cod-reduction-in-wastewater/

Olayinka, O., Adedeji, O., Oladeru. (2013). Water quality and bacteriological assessment of slaughterhouse effluent on urban river in Nigeria. *Water Quality and Bacteriological Assessment of Slaughterhouse Effluent on Urban River in Nigeria*, *8*, 277–286.

Özel Duygan, B. D., Udert, K. M., Remmele, A., McArdell, C. S. (2021). Removal of pharmaceuticals from human urine during storage, aerobic biological treatment, and activated carbon adsorption to produce a safe fertilizer. *Resources, Conservation and Recycling*, *166*, 105341. https://doi.org/10.1016/j.resconrec.2020.105341

Putnam, D. F. (1971). *Composition and Concentrative Properties of Human Urine*. National Aeronautics and Space Administration. Retrieved May 30, 2023, from https://ntrs.nasa.gov/api/citations/19710023044/downloads/19710023044.pdf

Pathania, D., Thakur, M., Sharma, A. (2020). Chapter 9—Photocatalytical degradation of pesticides. In P. Singh, A. Borthakur, P. K. Mishra, & D. Tiwary (Eds.), *Nano-Materials as Photocatalysts for Degradation of Environmental Pollutants* (pp. 153–172). Elsevier. https://doi.org/10.1016/B978-0-12-818598-8.00009-2

Papić, S., Vujević, D., Koprivanac, N., Šinko, D. (2009). Decolourization and mineralization of commercial reactive dyes by using homogeneous and heterogeneous Fenton and UV/Fenton processes. *Journal of Hazardous Materials*, *164*(2), 1137–1145. https://doi.org/10.1016/j.jhazmat.2008.09.008

Pignatello, J. J., Oliveros, E., MacKay, A. (2006). Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Critical Reviews in Environmental Science and Technology*, *36*(1), 1–84. https://doi.org/10.1080/10643380500326564

Pereira, A. C., Papini, R. M. (2015). Processes for phosphorus removal from iron ore—A review. *Rem: Revista Escola de Minas*, *68*, 331–335. https://doi.org/10.1590/0370-44672014680202

Perchlorates | Public Health Statement | ATSDR. (n.d.). Retrieved May 30, 2023, from https://wwwn.cdc.gov/TSP/PHS/PHS.aspx?phsid=892&toxid=181

Ray, H., Perreault, F., Boyer, T. H. (2019). Urea recovery from fresh human urine by forward osmosis and membrane distillation (FO–MD). *Environmental Science: Water Research & Technology*, *5*(11), 1993–2003. https://doi.org/10.1039/C9EW00720B

Rose, A. (2010). Advances in Passive Treatment of Coal Mine Drainage 1998-2009. *Journal American Society of Mining and Reclamation*, *2010*. https://doi.org/10.21000/JASMR10010847

Sarigul, N., Korkmaz, F., Kurultak, İ. (2019). A New Artificial Urine Protocol to Better Imitate Human Urine. Scientific Reports, 9, 20159. https://doi.org/10.1038/s41598-019-56693-4

Simha, P., Vasiljev, A., Randall, D. G., & Vinnerås, B. (2023). Factors influencing the recovery of organic nitrogen from fresh human urine dosed with organic/inorganic acids and concentrated by evaporation in ambient conditions. *Science of The Total Environment*, *879*, 163053. https://doi.org/10.1016/j.scitotenv.2023.163053

Simha, P., Deb, C. K., Randall, D. G., Vinnerås, B. (2022). Thermodynamics and Kinetics of pH-dependent Dissolution of Sparingly Soluble Alkaline Earth Hydroxides in Source-Separated Human Urine Collected in Decentralised Sanitation Systems. *Frontiers in Environmental Science*, *10*. https://doi.org/10.3389/fenvs.2022.889119

Simha, P., Lalander, C., Nordin, A., Vinnerås, B. (2020). Alkaline dehydration of source-separated fresh human urine: Preliminary insights into using different dehydration temperature and media. *Science of The Total Environment*, *733*, 139313. https://doi.org/10.1016/j.scitotenv.2020.139313

Senecal, J., Nordin, A., Simha, P., Vinnerås, B. (2018). Hygiene aspect of treating human urine by alkaline dehydration. *Water Research*, *144*, 474–481. https://doi.org/10.1016/j.watres.2018.07.030

Shetty, R., Verma, S. (2015). *Fenton's Reagent for the Treatment of Pharmaceutical Industry Wastewater*. https://www.semanticscholar.org/paper/Fenton%E2%80%99s-Reagent-for-the-Treatment-of-Industry-Shetty-Verma/300234d514397bd4cc08162ec3f330a5128be501

Sum Parameters: Potential and Limitations—ScienceDirect. (n.d.). Retrieved May 30, 2023, from https://www.sciencedirect.com/science/article/pii/B9780444531995000488

Saharan, V., Pinjari, D., Gogate, P., Pandit, A. (2014). Advanced Oxidation Technologies for Wastewater Treatment. In *Industrial Wastewater Treatment, Recycling and Reuse* (pp. 141–191). https://doi.org/10.1016/B978-0-08-099968-5.00003-9

Shen, Z., Li, J., Zhang, Y., Bai, J., Tan, X., Li, X., Qiao, L., Xu, Q., Zhou, B. (2019). Highly efficient total nitrogen and simultaneous total organic carbon removal for urine based on the photoelectrochemical cycle reaction of chlorine and hydroxyl radicals. *Electrochimica Acta*, *297*, 1–9. https://doi.org/10.1016/j.electacta.2018.11.087

THE 17 GOALS | Sustainable Development. (n.d.). Retrieved June 5, 2023, from https://sdgs.un.org/goals

Tarre, S., Green, M. (2004). High-Rate Nitrification at Low pH in Suspended- and Attached-Biomass Reactors. *Applied and Environmental Microbiology*, *70*(11), 6481–6487. https://doi.org/10.1128/AEM.70.11.6481-6487.2004

Urine 24-hour volume: MedlinePlus Medical Encyclopedia. (n.d.). Retrieved May 30, 2023, from https://medlineplus.gov/ency/article/003425.htm

Vinnerås, B., & Jönsson, H. (2002). The performance and potential of faecal separation and urine diversion to recycle plant nutrients in household wastewater. Bioresource Technology, 84(3), 275–282. https://doi.org/10.1016/s0960-8524(02)00054-8

Why Is My Urine Bright Yellow? Causes and Treatment. (2018, August 20). Healthline. https://www.healthline.com/health/bright-yellow-urine

Wang, J., Chu, L. (2016). Biological nitrate removal from water and wastewater by solid-phase denitrification process. *Biotechnology Advances*, *34*(6), 1103–1112. https://doi.org/10.1016/j.biotechadv.2016.07.001

Xu, M., Wu, C., Zhou, Y., Xu, M., Wu, C., Zhou, Y. (2020). Advancements in the Fenton Process for Wastewater Treatment. In *Advanced Oxidation Processes—Applications, Trends, and Prospects*. IntechOpen. https://doi.org/10.5772/intechopen.90256

Zhang, H., Choi, H. J., Huang, C.-P. (2005). Optimization of Fenton process for the treatment of landfill leachate. *Journal of Hazardous Materials*, *125*(1), 166–174. https://doi.org/10.1016/j.jhazmat.2005.05.025

APPENDICES

Appendix 1. (1)

Table 1. Shows the composition of different synthetic urine concentrations. (Simha et al., 2022)

Measure-ments	Cf 1 g/L	Cf 5 g/L	Cf 10 g/L
NaCl	0,04	0,2	0,4
Na_2SO_4	2,3	11,5	23
KCl	1,9	9,5	19
$MgCl_2.6H_2O$	0,24	1,2	2,4
NaH_2PO_4	0,6	3	6
$CaCl_2$	0,14	0,7	1,4
CH_4N_2O (Urea)	8,71	43,55	87,1
NH_4Cl	0,52	2,6	5,2
KOH	0,17	0,85	1,7
pH	6,97 unitless	6,97 Unitless	6,97 Unitless