



FACULTY OF TECHNOLOGY

ELECTROCHEMICAL WAYS TO UTILIZE WASTEWATER IN THE HYDROGEN ECONOMY

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PROCESS AND ENVIRONMENTAL ENGINEERING

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ABSTRACT

Electrochemical ways to utilize wastewater in the hydrogen economy

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Hydrogen is considered to be one solution for clean energy. A large portion of hydrogen is produced from fossil fuels. Electrolysis of water has been proposed as a greener solution. However, the climate change imposes constraints on water usage. This leads to competition in water use with industrial, agricultural, and consumer sectors. Therefore, water electrolysis may not necessarily be a universally suitable solution. It would be important to find alternative ways to produce hydrogen with maximum water efficiency.

Wastewater is an essential product, and its purification is very energy intensive. Currently nitrogen in wastewater is treated in a manner that nitrogen gas is released by bacteria back into the natural nitrogen cycle. This nitrogen could be utilized for hydrogen storage and production in a form of urea.

The purpose of this bachelor's thesis is to review the use of urea and ammonia contained in wastewater in the hydrogen economy. First, properties of urea and ammonia are explored. Then the composition of wastewater is examined. Additionally, the current wastewater treatment technology is presented focusing on nitrogen removal techniques. The electrochemical reactions are also presented focusing on urea.

The results indicate that focus should be turned from catalyst materials into different kinds of pilot projects. The problems of the hydrogen economy also apply to the electrochemical treatment of wastewater. The growing amount of renewable energy and hydrogen infrastructure could realize the potential of electrochemical treatment of wastewater to produce green hydrogen and urea.

Keywords: Hydrogen, Electrolysis, Urea, Ammonia, Wastewater, Hydrogen economy

TIIVISTELMÄ

Jäteveden sähkökemiallinen hyödyntäminen vetytaloudessa

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Vetyä pidetään yhtenä ratkaisuna puhtaan energian kysyntään. Suuri osa vedystä tuotetaan fossiilisista polttoaineista. Puhtaammaksi ratkaisuksi on tarjottu veden elektrolyysiä. Lämpivä ilmasto asettaa rajoitteita globaalille veden käytölle. Vähenevästä veden määrästä kilpailee teollisuus-, maatalous- ja kulutussektori. Tämän takia veden elektrolyysi ei välttämättä sovellu yleiseksi ratkaisuksi. Olisikin tärkeää löytää vaihtoehtoisia tapoja tuottaa vetyä mahdollisimman vesitehokkaasti.

Jätevesi on välttämätön tuote, jonka puhdistaminen on hyvin energiaintensiivistä. Tällä hetkellä jäteveden typenpoistossa typpikaasu vapautuu bakteereiden aineenvaihdunnan seurauksena takaisin luonnolliseen typenkiertoon. Tämä typpi voitaisiin valjastaa vedyn varastointiin ja tuotantoon.

Tämän kandidaatintyön tarkoituksena on selvittää jäteveden sisältämän urean ja ammoniakkin käyttöä vetytaloudessa. Työssä tutustutaan urean ja ammoniakkin ominaisuuksiin. Tämän jälkeen käydään läpi jäteveden ominaisuuksia. Työssä perehdytään lisäksi nykyiseen jätevedenpuhdistustekniikkaan. Etenkin käsitellään nykyisin jätevedenpuhdistuksessa käytettävää typenpoistotekniikkaa ja tarkastellaan elektrolyysin vaikutusta prosessiin.

Työn keskeisin tulos on, että tutkimuksessa tulisi siirtyä käytännön pilottihankkeisiin. Vetytalouden yleiset ongelmat koskevat myös jäteveden sähkökemiallista käsittelyä. Uusiutuvan energian määrän kasvaessa ja vetytalouden kehittyessä jäteveden sähkökemiallinen käsittely voi mahdollistaa sekä puhtaan vedyn että urean tuottamisen.

Asiasanat: Vety, Elektrolyysi, Urea, Ammoniakki, Jätevesi, Vetytalous

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LIST OF ABBREVIATIONS

ATP	adenosine triphosphate
ADP	adenosine diphosphate
e-UOR	electrocatalytic urea oxidation reaction
FE _x	Faraday efficiency of x
GHG	greenhouse gas
HB	Haber-Bosch
HER	hydrogen evolution reaction
LOC	liquid hydrogen carrier
LOHC	liquid organic hydrogen carrier
OER	oxygen evolution reaction
PCET	proton-coupled electron transfer
RHE	reversible hydrogen electrode
UOR	urea oxidation reaction
WWTP	wastewater treatment plant

1 INTRODUCTION

Green hydrogen has been proposed as a potential alternative to expanding energy demand flexibility. Green hydrogen is produced by the electrolysis of water using renewable energy. Traditional water electrolysis is usually carried out in acidic or alkaline conditions to alleviate charge transport losses in electrochemical processes. Electrochemical water splitting requires 1.23 V thermodynamic potential in standard conditions. Practical electrolyzers use much higher voltage because both hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode are slow and require high overpotentials to reach reasonable current densities. Transition metal-based catalysts can be utilized in alkaline media: stainless steel electrodes for OER and Ni for HER. Acidic conditions corrode transition metals so noble metal-based catalysts are used instead. Large scale hydrogen production faces problems with noble metal-based catalysts being costly, scarce, and unstable. The activity of noble metal-free catalyst is only mediocre. (You and Sun 2018)

Anodic oxygen evolution can be replaced with more oxidizable species. Ammonia, methanol, ethanol, glycerol, and urea have been tested. Compared to the traditional route such compounds allow electrolysis at potentials under 1 V. This leads to advantages in terms of efficiency and economy. (Chen et al. 2014)

Other problems facing hydrogen-based energy systems include lack of infrastructure, mainly storage and transportation problems. Hydrogen gas has very low volumetric energy density. Liquified hydrogen has better volumetric energy density, but liquification requires extremely low temperatures. Boil-off from Dewars also limits longer storage. Liquid hydrogen carriers (LHC) are molecules that store hydrogen in chemical bonds. They are seen as a solution to store and transport hydrogen. Ammonia and liquid organic hydrogen carriers (LOHCs) such as urea are stable for long period of time and can use existing infrastructure to store and transport hydrogen. (Autrey and Chen 2023)

Urea synthesis is a mature chemical process. Traditionally it is linked to compliment the ammonia production plant since ammonia acts as a reactant for urea synthesis. Ammonia is produced in Haber-Bosch (HB) reaction from hydrogen and nitrogen. 96% of commercially produced hydrogen comes from fossil fuels mainly from natural gas, coal, or oil. Using fossil fuels as feedstock produces carbon dioxide (CO₂) alongside with

hydrogen. Both ammonia and urea syntheses are energy intensive processes. Urea and ammonia are responsible for 0.93% of the total global greenhouse gas (GHG) emissions (Milani et al. 2022; Masjedi et al. 2024).

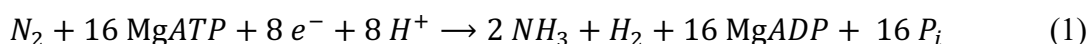
Urea and ammonia are both common nitrogen species in wastewater. European union is currently updating its legislation concerning urban wastewater treatment. New directive proposes to tighten nitrogen removal requirements rising from current 70 % up to 85 %. Another major change in directive concerns temperature of sewage. Current directive requires nitrogen removal only if the temperature of wastewater is over 12°C. In new proposal this temperature limit is removed (European Commission 2022). If the directive is approved as it is proposed, it will have a major impact on Finnish wastewater processing requirements since most of current processing plants do not meet the new requirements. (Henri Haimi 2023)

Wastewater treatment of nitrogen and production of hydrogen could be coupled via the electrocatalytic urea oxidation reaction (e-UOR). Research on e-UOR started in the 1970s with noble metal catalysts. Low efficiency and high price of noble-metal catalysts have promoted non-noble metal catalyst research. Structure of urease enzyme inspired research on nickel-metal based catalysts. Other transitional metal-based catalysts have shown promising performance. Electrocatalysis can be performed under ambient conditions using green energy. Utilization of e-UOR with green energy in wastewater treatment would also serve as sustainable and environmentally friendly technology to remove nitrogen and produce hydrogen. Electrochemical ways can also be utilized to produce urea from wastewater (Hu et al. 2024). (Gao et al. 2024)

The goal of this thesis is to investigate the possibility to utilize wastewater as a green urea source to promote green hydrogen economy. First properties of ammonia and urea are assessed. Wastewater is covered in a general level going more in detail with chemical constituents in wastewater. Current wastewater treatment technologies are also presented. The literary review consists of current results in electrochemical research on reactions of urea and their possibilities to be utilized in wastewater treatment, urea, and hydrogen production. Lastly, possible practical applications in energy and environmental fields are discussed.

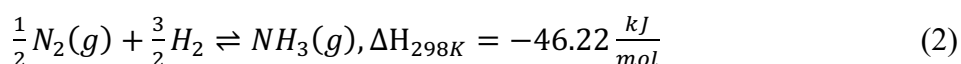
2 AMMONIA

Ammonia is a natural and common nitrous agent (Appl 2011). It is formed naturally in nitrogen fixation in which molecular nitrogen and hydrogen from water is combined into ammonia. Biological nitrogen fixation occurs only in certain bacteria such as cyanobacteria. The reaction is described here below (1). (Marschner 2012, p. 391)



It uses water as a hydrogen source and is catalyzed by nitrogenase enzyme. Enzyme's active site contains molybdenum and vanadium. Biological reduction of nitrogen gas into ammonia is highly energy demanding process. (Marschner 2012) Energy to the reaction is given by hydrolysis of phosphate groups (P_i) in adenosine triphosphate (ATP). This converts ATP into adenosine diphosphate (ADP). In animal metabolism ammonia is a toxic waste product. It is converted to non-toxic substances such as urea. Fish and aquatic invertebrates can excrete ammonium directly to water (Heino and Vuento 2007, pp. 151–152).

Ammonia synthesis is an exothermic reaction between nitrogen and hydrogen (2)(Appl 2011).



Ammonia was produced 235 million tons worldwide in 2019. More than 90 % of industrially ammonia is produced in Haber-Bosch (HB) process. HB process is very energy intensive mostly due its high operating pressure and temperature. Energy to the process is generally taken from fossil fuels and 96 % of hydrogen used in the synthesis reaction is also derived from fossil fuels. HB is one of the most GHG emitters responsible for 1.2% of the global anthropogenic CO₂ emissions. (Ghavam et al. 2021)

2.1 Properties of ammonia

Ammonia (NH_3) has molecular mass of 17,03 g/mol and it has a hydrogen content of 17,8 wt%. Other properties are listed in table 1.

Table 1. Properties of Ammonia (Appl 2011)

Property	Value
Melting point, °C	-77,71
Boiling point, °C	-33.43
Density, g/dm ³ , 0°	0,7714

At room temperature and atmospheric pressure ammonia is a colorless gas that has a pungent odor. It has relatively high boiling point of -33°C and thus can be liquidized easily. The flammable limits of ammonia in air are 16-27% by volume in air. The ignition temperature in such mixtures is approximately 650°C. Ammonia is highly soluble in water and the reaction is very exothermic. Approximately 2018 kJ of heat is evolved when 1 kg ammonia gas is dissolved into water. It is also good solvent for salts and organic compounds (Pattabathula 2019). (Appl 2011)

2.2 Ammonia as a hydrogen carrier

Ammonia has a high hydrogen storage capacity by volume and by mass. It has a high ignition point making it safe for transportation. Ammonia can be catalytically cracked in reverse of reaction (2) to produce hydrogen and nitrogen. Reaction is highly endothermic and occurs in the range of 400-900°C making it very energy intensive. Produced hydrogen can be utilized in hydrogen fuel cells. Purity requirements of hydrogen for polymers electrolyte membrane fuel cell is 99.97 mol%. This requires purification of cracked ammonia. (Ashcroft and Goddin 2022)

3 UREA

Urea was the first organic compound to be synthesized from inorganic substance by Friedrich Wöhler in 1828. It can be seen as a starting point of modern organic chemistry. Urea also is a final product of mammalian nitrogen metabolism, and it is excreted as part of urine. Adult human produces on an average 25-30 g of urea per day. (Brouwer 2019)

3.1 Properties of urea

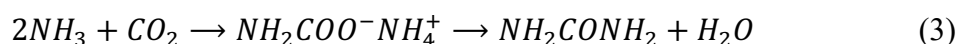
Urea $CO((NH_2)_2)$ has molecular mass of 60.06 g/mol and it has hydrogen content of 6.7 wt%. Other properties are listed in table 2.

Table 2. Properties of Urea (Brouwer 2019)

Property	Value
Melting point, °C	133-134
Boiling point, °C	Decomposes
Density, g/cm ³	1.32
Solubility in water, g/100g (at 20° C)	51.6

At room temperature and atmospheric pressure urea is stable colorless, odorless, and tasteless. In pure form it forms crystalline solid, and it can be easily pressed into granules or pellets. Urea is highly soluble in water. In water solution it is non-toxic and acts as a weak base. (Brouwer 2019)

Urea is produced industrially in Bosch-Meiser urea process described in reaction (3). It requires ammonia and carbon dioxide at elevated temperature and pressure. (Brouwer 2019)



Mammals produce urea as a waste product of nitrogen metabolism. Urea is produced in liver in several biochemical steps called the urea cycle (Heino and Vuento 2007, p. 152). Kidneys extract urea from bloodstream and excrete it as urine. In water solution, urea

slowly hydrolyses into ammonia and carbon dioxide. Reaction is catalyzed by ureases enzymes that are found in numerous bacteria, plants, fungi, algae, and some invertebrates. It is also present in soil as a soil enzyme (Krajewska et al. 2012).

3.2 Urea as a hydrogen carrier

Urea has a hydrogen content of 6.7 wt% so it would be a suitable candidate for a hydrogen carrier. Table 3 shows properties of hydrogen and hydrogen carriers. High flammability and toxicity are common to all except for urea. Only levels above several thousand mg/liter it may become toxic to animals. Ethanol and methanol can be produced from carbon-neutral bioresources and are best processed to engine fuels to reduce carbon emissions. (Rollinson et al. 2011)

Table 3. Properties of hydrogen carriers. Adapted from (Rollinson et al. 2011)

Substance	H (wt%)	GHS Classification (pictograms)	Toxicity TLV	Flammability in air	Melting Point (°C)	Boiling point (°C)
Ammonia (NH ₃)	17.65	04,05,06,09	25 ppm as TWA	Auto-ignition temperature: 630°C Explosive limits, vol% 15-33	-78	-33
Cyclohexane	14.4	02,07,08,09	100 ppm as TWA	Auto-ignition temperature: 260°C Explosive limits, vol% in air: 1.3-8.4	7	81
Hydrogen (H ₂)	100	02,04	Asphyxiant in high concentrations	Auto-ignition temperature: 560°C Explosive limits, vol% in air: 4-75	-259	-253
Methanol (CH ₃ OH)	12.5	02,06,07	200 ppm as TWA	Auto-ignition temperature: 440°C Explosive limits, vol% in air: 6-50	-98	65
Urea (NH ₂) ₂ CO	6.71	None	None	Non-flammable	Crystalline solid Decomposes at 133°C	

note. Data in the table is updated from ICSC database. Classification in the original table is changed to depict current GHS pictograms. GHS pictograms 01 = exploding bomb, 02 = flame, 03 = flame over circle, 04 = gas cylinder, 05 = corrosion, 06 = skull and crossbones, 07 = exclamation mark, 08 = health hazard, 09 = environment

Stable and lightweight crystalline form at atmospheric conditions make urea easy to storage and transport. Heating and enzymatic hydrolysis causes urea to decompose in reverse reaction of (3) into ammonia and CO₂. Spontaneous decomposition to ammonia

is very slow process. Half-life times are estimated to be over 40 years at 25°C. (Rollinson et al. 2011)

Controlled ammonia evolution from urea could be considered as a favorable reaction since ammonia can be used directly in alkaline and solid oxide fuel cells. reverse of reaction (2) in a process called cracking. (Rollinson et al. 2011)

3.3 Ureases

Ureases catalyze the hydrolysis of urea into ammonia and carbon dioxide. They occur naturally in plants, bacteria, yeasts, and fungi. Structurally, ureases are mostly similar, but their biological activities differ significantly. For example, plant ureases can also act as pesticides. (Balasubramanian and Ponnuraj 2010)

Plant and fungal ureases are homo-oligomeric proteins, while bacterial ureases are multimers of two or three subunits. Active site of ureases contains two nickel (Ni^{2+}) ions, which are bridged by a hydroxyl group and a carbamylated lysine (Svane et al. 2020). Binding of nickel in the structure is tight and differs from most other metalloenzyme. Removal of metal ion can be achieved by harsh treatments with acids. (Balasubramanian and Ponnuraj 2010)

3.3.1 Urease inhibition

Working of urease can be prevented by acid addition (Hellström et al. 1999), alkaline addition (Randall et al. 2016), using electrochemical treatment (Ikematsu et al. 2007) or by inhibitors (Svane et al. 2020).

The optimal pH conditions for bacterial ureases ranges between 6.8-8.7 (Moblely and Hausinger 1989). Acid and alkaline addition cause unfavorable conditions for survival of bacteria. In acidic conditions the number of bacteria is small at pH below 3 (Hellström et al. 1999). On the other end, 30-minute exposure of wastewater to pH level higher than 11.5 will reduce the amount of bacteria to negligible numbers (Randall et al. 2016).

Urease can be inactivated by electrochemically produced chlorine when oxidation-reduction potential is maintained at 240 mV or above. Incubation times over 2 hours

causes the changes in the activity to be irreversible. This is probably caused by unfolding of the protein structure. (Ikematsu et al. 2007)

Inhibitors can be placed into three categories. In the first category inhibitor binds directly into the enzyme's active site. The second category binds covalently to enzyme changing its structure. The third category consists of metal ion chelators. They sequester the nickel ions which inhibits the formation of the active site.(Svane et al. 2020)

Commonly known inhibitors include thiols, hydroxamic acids, phosphates, amides and esters of phosphoric acids, fluoride, quinones, heavy metal ions, and polyphenols.(Kappaun et al. 2018)

Svane et al. tested the effects of 71 commercially available compounds on ureolytic activity with *Klebsiella pneumoniae* bacteria and jack bean urease. They found 30 compounds that inhibit urease in some level. The results showed the importance of choosing an anti-ureolytic compound according to intended purpose. For example, livestock manure contains relatively high concentrations of metal ions. Nickel chelators are not suitable when high concentrations of metal ions are present. (Svane et al. 2020)

4 WASTEWATER

Wastewater is commonly characterized in terms of its physical properties and its chemical and biological constituents. Wastewater is a mix of human feces and urine, bath water, food waste, personal and household maintenance products and wide range of inorganic and organic compounds in trace amounts. (Metcalf & Eddy et al. 2014, p. 60)

4.1 European law

Terms concerning wastewater and its treatment are established in EU law. According to article 2 in council directive concerning urban wastewater treatment (Directive 91/271 2024):

- ”1. ‘urban waste water’ means domestic waste water or the mixture of domestic waste water with industrial waste water and/or run-off rain water;
2. ‘domestic waste water’ means waste water from residential settlements and services which originates predominantly from the human metabolism and from household activities;
3. ‘industrial waste water’ means any waste water which is discharged from premises used for carrying on any trade or industry, other than domestic waste water and run-off rain water;”

4.2 Physical properties

Most important physical characteristics are total solids, particle size distribution, turbidity, color, transmittance, temperature, and conductivity. Physical properties are a combination of natural and anthropogenic origin. Natural water is an important starting point since it inherently determines specific gravity and weight. Temperature is also defined by the combination of surface water and groundwater as well as location. Other properties are derived from discharges. (Metcalf & Eddy et al. 2014, p. 73)

The temperature of wastewater is usually higher than of the local water supply because of discharges of warm water from municipal and industrial sources. The temperature of

wastewater is important because of its effect on chemical reaction and rates and bacterial efficiency. Optimal temperature for biological activity ranges from 25° to 35°C. (Metcalf & Eddy et al. 2014, pp. 87–88)

A project led by Helsingin seudun ympäristöpalvelut (HSY) gathered monthly averages of wastewater temperature in three different waste water treatment plants (WWTP) in southern Finland. The monthly averages varied between 9° and 20° C. (Ahonen 2021)

4.3 Chemical properties

Wastewater contains organic and inorganic chemical components. Inorganic chemical components include nutrients, metallic and nonmetallic constituents, and gases. Alkalinity and pH are considered to be inorganic properties. Common concentrations of some chemical components in municipal wastewater are presented in table 4. Organic compounds typically are proteins, carbohydrates, and oils and fats. Because urea decomposes rapidly, it is usually only found in fresh wastewater. (Metcalf & Eddy et al. 2014, p. 90)

Table 4. Common concentrations of chemical components in municipal wastewater. Adapted from (Karttunen et al. 2004, p. 494)

Substance	Concentration (mg/l)
Total phosphorus	6-8
Total nitrogen	25-40
Ammoniacal nitrogen	15-25
Chlorides	25-75
Potassium	10-15
pH	6-8

4.3.1 Nitrogen

Nitrogen compounds in wastewater originate from animals, sodium nitrate and atmosphere. The chemistry of nitrogen is complex since it can assume various oxidation states in different conditions. The oxidation states are summarized in table 5.

Table 5. The oxidation states of nitrogen (Sawyer et al. 2003)

Oxidation state	-III	0	I	II	III	IV	V
Substance	NH ₃	N ₂	N ₂ O	NO	N ₂ O ₂	NO ₂	N ₂ O ₅

Common forms of nitrogen in wastewater are ammonia (NH₃), ammonium(NH₄⁺), nitrogen gas (N₂), nitrite (NO₂⁻), and nitrate (NO₃⁻). The organic compounds containing nitrogen can be soluble or particulate. They are effectively turned into ammonia by microorganisms. Urea in wastewater is readily converted into ammonium carbonate and finally into ammonia. (Metcalf & Eddy et al. 2014, pp. 92–96)

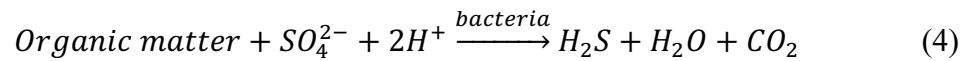
4.3.2 Inorganic nonmetallic constituents

Phosphorus in wastewater can be classified into particulate and dissolved. Both can be either in reactive or in nonreactive form. The soluble nonreactive forms are of great interest since they are not easily removed by current wastewater treatment processes. Municipal wastewaters typically contain from 3.7 to 11 mg/l of phosphorus. (Metcalf & Eddy et al. 2014, p. 96)

The pH is an important parameter for wastewater since many other chemical constituents are dependent on it by chemical reactions. Suitable pH for most biological life is between 6 and 9. This is important since biological wastewater treatment becomes difficult in extreme pH conditions. (Metcalf & Eddy et al. 2014, p. 90)

Chlorides can affect the final reuse of treated wastewater since traditional wastewater treatment methods do not remove them. Sources can be natural like seawater intrusion in coastal areas. Daily human excreta contain about 6 grams of chlorides per person.(Metcalf & Eddy et al. 2014, pp. 91–92)

The sulfate ion (SO_4^{2-}) occurs naturally in most water supplies. Bacteria under anaerobic conditions can utilize sulfate in their metabolism turning sulfate into hydrogen sulfide (H_2S). Process is generally depicted in reaction (4).



Hydrogen sulfide gas diffuses into the headspace above wastewater. It can be oxidized biologically into sulfuric acid causing corrosion in the sewerage. (Metcalf & Eddy et al. 2014, pp. 97–98)

Other common gases in addition of hydrogen sulfide in wastewater are nitrogen, oxygen, carbon dioxide, ammonia, and methane. Solubility of slightly soluble gases follow Henry's law (5):

$$p_g = \frac{H}{P_T} x_g, \quad (5)$$

where p_g is mole fraction of gas in air
 H is Henry's law constant [atm]
 P_T is total pressure [atm]
 x_g is mole fraction of gas in water

As highly soluble substances ammonia and CO_2 do not follow Henry's law. (Metcalf & Eddy et al. 2014, pp. 98–100)

Oxygen is required for the respiration of aerobic microorganisms. Its presence is desired because it can be utilized in biochemical treatment of wastewater, and it prevents anaerobic bacterial metabolism that leads to formation of noxious odors. (Metcalf & Eddy et al. 2014, pp. 102–103)

Methane (CH_4) in wastewater is product of anaerobic decomposition of organic matter. It is a colorless, odorless, and combustible hydrocarbon. It may cause explosion hazard if sewer system is not properly ventilated. Methane is also serious GHG with 25 times bigger impact than that of CO_2 . (Metcalf & Eddy et al. 2014, p. 103)

5 WASTEWATER TREATMENT OF NITROGEN

In water systems excess amounts of nitrogen and phosphorous cause eutrophication. Leaching of nitrogen and phosphorus from forests and farmland is the primary source of eutrophication. (VanLoon and Duffy 2017, pp. 351–356, 394) Discharges from municipal wastewater treatment plants, industrial activities and small wastewater systems add to the effect. Discharges are regulated by EU's The Urban Waste Water Treatment Directive and it stands as a basis for minimal efficiency in nitrogen removal. (Karttunen et al. 2004, p. 492)

5.1 Wastewater treatment plant

Survey conducted by Finnish Environment Institute found that most common assembly of wastewater treatment plant in Finland consists of following steps. First the sewage is screened to separate rags and other larger object. Next sand, gravel and other heavier particles are removed in the grit chamber. Pre-aeration is only used in larger facilities, but preliminary sedimentation is also included in mid-sized units. Purpose is to remove excess organic matter before the actual aeration and prepare the sewage for biological processing. The most common biological method used is activated sludge process in which phosphorus is simultaneously chemically precipitated. Precipitation is done by adding aluminum or iron salts during preliminary sedimentation. Another common practice is to add precipitation agents as a two-point addition in the beginning and right before post-sedimentation. Post-sedimentation is used in every plant unless biological process includes biological filters. In biological filters bacteria are used to improve primarily nitrogen removal as a post-treatment. Other common post-treatment processes are flotation, sand filtering, final clarification. Sanitation is also used when necessary. Survey did not gather information about use of sanitation process (Laitinen et al. 2014, p. 30)

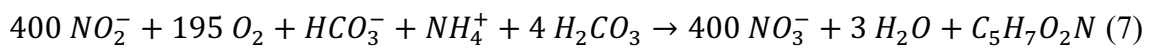
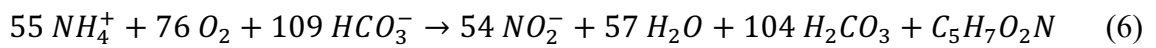
5.2 Nitrogen removal

In Finland nitrogen removal from wastewater is almost exclusively carried out by biological processing. Activated sludge process is the most common practice (Laitinen et al. 2014, p. 43). It consists of two main reactions: nitrification and denitrification.

Microbes that purify wastewater live in the biomass of the activated sludge. As microbiological processes they both require very specific conditions, which differ completely from another. At the end of process nitrogen is released in gaseous form (N_2) and some is assimilated in the sludge. (Karttunen et al. 2004, p. 211)

5.2.1 Nitrification

First step in the process is nitrification. Nitrification is not actually nitrogen removal. Its purpose is to convert nitrogen into more processable form into nitrate. Partial reactions are depicted in reactions (6) and (7). In nitrification ammoniacal nitrogen is first converted into nitrite (6) and finally into nitrate (7). $C_5H_7O_2N$ in equations represents nitrogen trapped in the sludge.

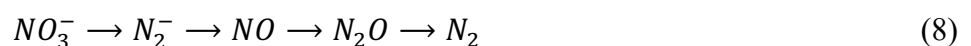


From equations (6) and (7) can be determined that one ammonium nitrogen gram requires 4.6 g oxygen and alkalinity decreases 8.64 mg HCO_3^- per oxidized ammonium nitrate milligram.

Ideal temperature for the reaction is between 30°C and 35°C and pH range from 7.5 to 8.6. The reaction rate will drop drastically if ideal conditions are not maintained. Reaction rate is also slowed by certain kinds of inhibitors. Their amount in wastewater is monitored by various tests. (Karttunen et al. 2004, pp. 211–212)

5.2.2 Denitrification

In denitrification nitrate is converted into nitrogen gas. Denitrification is an anoxic reaction that uses nitrate as an electron receiver. Denitrification bacteria are heterotrophic, and they need an external carbon source to support their metabolism. Process consists of multiple steps that are simplified in equation (8). (Karttunen et al. 2004, p. 213)



Oxygen inhibits enzymes in reaction. Optimal pH ranges from 7 to 8 and alkalinity is increased. When all organic carbon is consumed denitrification covers around 50 % of

decrease in alkalinity caused by nitrification. One gram of removed nitrogen requires 3 to 6 grams of organic matter measured in BOD. (Karttunen et al. 2004, p. 213)

5.2.3 Energy consumption of activated sludge process

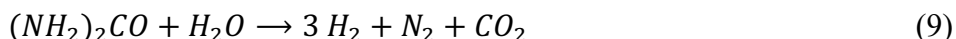
Wastewater treatment process consumes 80 % of treatment plants total energy. Roughly 56 % of that energy is used in aeration that is a key component in activated sludge process (Mikola et al. 2016)

Nitrification bacteria need oxygen for their metabolism. In atmospheric pressure oxygen in air is not soluble enough to keep activated process efficient. Aeration is required to keep process functioning. Energy consumption of activated sludge with nitrification and denitrification per wastewater volume treated is 0.23 kWh/m³.(Metcalf & Eddy et al. 2014, pp. 419, 1812)

6 ELECTROCATALYTICS REACTIONS OF UREA

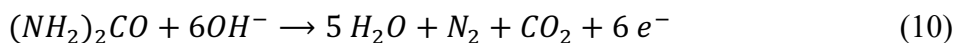
6.1 Urea oxidation reaction

Urea electrolysis could be utilized in wastewater treatment since it allows simultaneous hydrogen production and nitrogen removal from urea rich wastewater. Overall equation of urea electrolysis is depicted in reaction (9). (Yu et al. 2018)



Nitrogen gas can be collected from anode representing nitrogen removal of wastewater and hydrogen gas correspondingly from cathode.

Replacing anodic OER of traditional water splitting with urea oxidation reaction (UOR) can lower the thermodynamic equilibrium potential from 1.23 V to 0.37 V (Zhou et al. 2024). Similar problems to OER with slow reaction rates lie in the anodic urea oxidation reaction (UOR) depicted in reaction (10). (Yu et al. 2018)



6.2 Electrocatalytic urea oxidation reaction

Extensive studies have been conducted on electrocatalytic urea oxidation reaction (e-UOR). Typically, they are focused on catalyst materials. Mechanism and reaction pathways of UOR are still controversial and practical applications in energy and environmental fields are indefinite (Gao et al. 2024).

The e-UOR is a multi-proton-coupled electron transfer (PCET) and much more complex than conventional electrochemical reactions such as OER and HER (Gao et al. 2024). Transfer process of multiple electrons needs highly active catalysts to promote reaction rate during UOR. Noble metals such as platinum and rhodium can be used as catalysts. Unfortunately, use of noble metals in large-scale is unprofitable due the low efficiency and high material cost. Multiple candidates for inexpensive UOR catalysts have been in recent research including two dimensional MnO_2 crystals, metallic Ni (OH)₂ nanosheets and Ni-Mo based nanostructures. (Yu et al. 2018)

6.2.1 Noble metal catalysts

Noble metal-based catalysts are used in acidic and neutral environment. In acidic medium urea is slowly hydrolyzed generating ammonia and intermediates *NH_2CO or *NH_2COO . C-N bond in intermediates is broken down by electrophilic attack of a chemisorbed hydrogen in the surface of the catalyst. Ammonia formed from these processes goes through another N-N bond coupling forming gaseous nitrogen or it oxidizes into NO_x . $^*CO/CO_2$ species formed in the reaction are desorbed from the catalyst surface by the oxidation potential. (Gao et al. 2024)

In neutral and saline conditions chloride ions (Cl^-) take part in UOR in a mechanism called Cl-mediated UOR. Catalyst can be made from Pt, Ru, Ir and Ti metals as well as metal oxide-based metals and boron-doped diamond. Possible products for Cl^- are Cl_2 , OCl^- , $HOCl^-$ and chlorine radicals. All of them can act as a reactive species in UOR that have positive impact on reaction. Negative effects of Cl-mediated UOR are formation of by-products such as chloramine and oxychlorides. Chlorine evolution reaction (CER) also competes with UOR. (Gao et al. 2024)

Other natural impurities of urine such as SO_4^{2-} and phosphates also affect the UOR. High ratio of these ions compared to urea concentration reduces urea adsorption to catalyst surface by competition. (Gao et al. 2024)

6.2.2 Nickel catalysts

Nickel hydroxide $Ni(OH)_2$ is generally used under alkaline conditions because they are unstable and vulnerable in acidic and neutral conditions. There are two possible mechanisms for alkaline UOR that both suggests that the real active species in the reaction is $NiOOH$. UOR kinetics and stability is still poor due the complex nature of multi-PCET reaction. Recent studies have also found that reaction also generates NO_2^- , NO_3^- and N_2O as a secondary pollution. Nickel catalysts also suffer from competition of the OER when potential is raised over 1.5 V vs RHE. It was found that OH^- adsorption is related to a series of PCET reactions cleaving C-N bond in urea molecules to facilitate the UOR. High potential ($>1.5V$) leads to excessive adsorption of OH^- to active sites increasing OER. Research team found that modifying nickel-based catalyst with sulfur oxyanion they could not only inhibit adsorption of OH^- but also promote cleavage of C-N bond in urea molecules to boost UOR. (Gao et al. 2024)

Worcester Polytechnic Institute researchers found very promising catalyst consisting of synergistically interacted cobalt and nickel atoms with special electronic structures for selective UOR. (Zhou et al. 2024)

6.3 Urea synthesis by electrolysis of carbon dioxide and nitrate

Urea is industrially synthesized in a reaction (3) that requires harsh conditions and high energy input. Research efforts have been made to develop electrochemical synthesis routes. One possible route is co-reduction of CO_2 and NO_3^- . Reaction route is complex consisting of 16 electron transfers. This leads to various by-products and to low urea production efficiency. (Hu et al. 2024)

Ways to improve reaction is to design electrocatalyst to reduce the energy barrier of C-N coupling. Although better understanding of C-N mechanism Faraday efficiency of urea (FE_{urea}) is still limited. Local concentrations of reactants have effect on reaction rate. By research it is anticipated that high local concentrations of CO_2 and NO_3^- could promote urea production. (Hu et al. 2024)

Research team found that using pulsating potentials instead of static potential increased urea production. Using pulsating potentials between -0.2 and -0.8 versus RHE promoted C-N coupling because pulsated electrolysis inhibited local pH increase and therefore enhanced local CO_2 and NO_3^- concentrations near the catalysts surface. Using iron tetraphenylporphyrin (Fe-TPP) catalyst energy consumption was 44.62 kWh per produced urea kilogram with maximum FE_{urea} of 27.70 %. Efficiency was specifically enhanced by using PdCu catalysts resulting a maximum FE_{urea} of 70.36 % and energy consumption of 16.50 kWh per produced urea kilogram. (Hu et al. 2024)

7 DISCUSSION AND CONCLUSIONS

Urea has many favorable attributes. It is non-toxic, stable and can be pressed into granules. It can be used directly as a fertilizer, and it provides means of supplying both ammonia and hydrogen. It can also be utilized in direct fuel cell.

Current production of urea is very energy intensive and relies heavily on fossil fuels producing vast amounts of GHG emissions. Electrochemical ways to utilize nitrogen supply of wastewater could be coupled with variable renewable energy to provide a sustainable energy supply for urea production.

Supply of wastewater is the most important factor. The urea in current sewage system readily hydrolyses into ammonia and then oxidizes into nitrites and nitrates. To be efficient e-UOR requires transformation of these nitrogen compounds back to urea. Phosphates present in the wastewater also have negative effect on e-UOR kinetics. In current wastewater treatment process phosphates are precipitated before nitrogen removal. This is also beneficial to e-UOR utilization. Cold water temperature in Finnish environment could pose a problem. Catalyst material tests are commonly conducted at 25°C.

Another possibility to use wastewater is to link currently used activated sludge process with urea synthesis by electrolysis of carbon dioxide and nitrate. The nitrate is produced as a part of activated sludge process during nitrification step. This urea could be utilized in e-UOR. The urea could also be extracted for other uses. Another separation step would be needed to extract produced urea. This method increases the cost of wastewater treatment since nitrification is energy intensive and electrolysis process would add to that energy cost. Also, additional separation step adds to this cost. Benefits of this approach would be no need for a new sewage system. This scenario would be feasible only if there is a market for green urea and plenty of cheap renewable energy.

Another way to solve problems with temperature, phosphates and urea content could be solved by separating urine from other sewage and treating it on-site. Urine stream could be isolated, and working of urease could be inhibited by electrochemical treatment or using inhibitors. Transportation of pretreated urine is a big issue. Transportation through centralized sewer system nullifies the pretreatment process and installation of new

separate pipelines would require massive investments. Decentralized system of urine electrolyzers that convert urea directly into hydrogen could be a solution. This solution faces problems in common with the hydrogen economy – transportation and storage of hydrogen is problematic. Decentralized urine electrolysis system would be reasonable if hydrogen pipelines are constructed as a part of the hydrogen economy and the produced hydrogen can directly be fed into the gas grid.

Based on this review, researchers have found many promising catalyst materials for electrochemical reactions of urea. To test new materials in practice different kinds of pilot projects should be given more attention. In addition, the role of sewage system and WWTPs should be rethought in the perspective of hydrogen economy.

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