Novel sludge treatment technology enhances toxic metal removal, pathogen reduction, sludge digestibility and dewaterability

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The activated sludge process (ASP) is a widely applied technology for biological wastewater treatment. The sludge production from the ASP is enormous and its management contributes typically 30 - 50% of the total operating costs of the wastewater treatment plant (WWTP). To develop a more cost-effective and sustainable wastewater treatment process, reduced sludge generation, improved energy recovery and beneficial biosolids reuse for nutrient recovery are key optimisation targets. Anaerobic digestion (AD) is widely adopted for sludge stabilisation and energy recovery through biogas production. However, the poor digestibility of sludge, especially waste activated sludge (WAS), often reduces the AD efficiency. Sludge application on agricultural land provides an opportunity for the beneficial reuse of organic matter and nutrients, particularly nitrogen and phosphorus. However, toxic metal contaminants, including Cd, Cr, Cu, Ni, Pb and Zn, often limit land application of these biosolids. Hence there is a significant demand for innovative sludge treatment solutions that can remove toxic metals and improve sludge digestibility to maximise the beneficial reuse potential and minimise costs related to transportation and disposal. In this thesis, a novel sludge treatment technology concept was developed with integrating nitrite addition and in situ electrochemical acid and alkali production, whereby metal removal, pathogen reduction, sludge digestibility and dewaterability were all enhanced at the same time.

First, the effect of nitrite addition on metal removal from acidified sludge was investigated using WAS from three different full-scale WWTPs. It was found that acidification to pH 2 by sulfuric acid achieved Zn removal of around 70%, but only 3 - 7% of Cu was removed. Nitrite addition of 20 mg NO$_2^-$-N/L (equal to 19.2 mg HNO$_2^-$-N/L) to the acidified WAS substantially enhanced Cu removal to 45-64%, while Zn removal was also increased to over 81%. Metal distribution analysis using sequential chemical extraction revealed that the improvement of Cu and Zn removal was mainly due to the release of the organically bound metal fraction. Subsequent process optimisation demonstrated that a nitrite addition of 10 mg NO$_2^-$-N/L and 5 hour exposure time was sufficient for metal removal enhancement for WAS at pH 2.

To avoid the purchase, transport, storage and handling of corrosive acid and alkali for the treatment as well as minimising possible occupational health and safety issues with the treatment, a three-compartment electrochemical system (ES) was employed for the in situ sludge acidification and alkali generation. Acidification (to pH 2) of WAS and alkali production were achieved in the anode and cathode compartment, respectively, with a current efficiency of 85% for both anode and cathode processes. Maintaining the optimised WAS treatment conditions (5 h at pH 2 with 10 mg
NO₂-N/L) achieved solubilisation of 60 ± 2% Cu and 86 ± 1% Zn, which is even higher than what was achieved in the treatment with external acid dosing. After separation of the solids by centrifugation, the metal-laden sludge liquor could be treated further in the cathodic process where the in situ generated alkali could be used to remove 74 ± 1% of Cu and 100% of Zn by precipitation.

To evaluate the effect of acidification with nitrite treatment on the digestibility of the treated sludge, biochemical methane potential (BMP) tests were conducted. WAS acidified to pH 2 by HCl dosing or electrochemical acidification was exposed to the optimised nitrite treatment, followed by removal of the solubilised metals by alkali precipitation. Compared to the untreated WAS, the methane production of the WAS treated by HCl or electrochemical acidification was increased by 46 ± 3% and 55 ± 6% through 69 days of BMP tests, respectively. By fitting the experimental data to a first-order kinetic model, the biochemical methane potential of WAS from the treatment by electrochemical acidification with nitrite and metal removal was estimated as 474 L CH₄/kg VS. Compared with the biochemical methane potential of 232 L CH₄/kg VS for the untreated WAS, this represents a very significant improvement of the WAS digestibility. Furthermore, the solids content of (laboratory-scale) belt filter dewatered sludge after treatment was increased from 14.6% to about 19%, which is again a very substantial and valuable improvement. Furthermore, a 4-log reduction in the concentration of two selected pathogen indicators, total coliforms and E.coli, was achieved in the WAS treated by acidification with nitrite addition.

A further application of the acid/nitrite method for the treatment of primary sludge was also evaluated. Only the electrochemical acidification method achieved a significant metal solubilisation (39 ± 1% and 82 ± 1% for Cu and Zn, respectively), but it had only a minor effect on the digestibility and dewaterability, both of which are typically quite high already for primary sludge.

At last, the economic potential of this novel sludge treatment technology concept was evaluated using a cost analysis based on the achieved research outcomes. The major economic benefits could be generated from reduced sludge production (through enhanced digestibility and dewaterability) and improved sludge quality (due to the decrease of toxic metal and pathogen concentrations). With both capital and operational cost considered, the electrochemical treatment with nitrite addition was estimated to be able to achieve a net benefit in 7 and 4 years for the sludge treatment with and without AD, respectively.

Overall, this study has clearly demonstrated the technical feasibility and economic potential of an innovative new sludge pre-treatment method that is able to achieve significantly improved metal
removal, pathogen reduction, sludge digestibility and dewaterability through a relatively simple, single stage treatment process involving acidification by ES and nitrite addition.
Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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This paper has been modified and incorporated as part of Chapter 3.

<table>
<thead>
<tr>
<th>Contributor</th>
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<tbody>
<tr>
<td>Du, Fangzhou (Candidate)</td>
<td>Conducted experiment (100%)</td>
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<td>Freguia, Stefano</td>
<td>Edited paper (5%)</td>
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<td>Yuan, Zhiguo</td>
<td>Designed experiments (10%)</td>
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<tr>
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<td>Edited paper (20%)</td>
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<td>Keller, Jürg</td>
<td>Designed experiments (20%)</td>
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<td>Pikaar, Ilje</td>
<td>Designed experiments (25%)</td>
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Contributions by others to the thesis

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# Table of contents

Abstract ........................................................................................................................... ii  
Acknowledgements .......................................................................................................... ix  
Table of contents .............................................................................................................. xii  
List of figures ................................................................................................................... xvi  
List of tables .................................................................................................................... xviii  
List of abbreviations ......................................................................................................... xix  
1. Introduction and literature review ............................................................................. 1  
   1.1 Introduction ............................................................................................................. 1  
   1.2 Literature review .................................................................................................... 3  
      1.2.1 Sludge production, reuse and regulation ......................................................... 3  
      1.2.2 Toxic metals removal from sludge ..................................................................... 6  
      1.2.3 Anaerobic digestion of sludge .......................................................................... 10  
      1.2.4 Nitrite application in wastewater industry ..................................................... 13  
      1.2.5 Electrochemical system in wastewater industry ........................................... 15  
      1.2.6 Knowledge gaps ............................................................................................. 16  
2. Research objectives and thesis overview .................................................................. 17  
   2.1 Research objectives and questions ......................................................................... 17  
      2.1.1 Use nitrite to enhance toxic metal removal from sludge ................................. 17  
      2.1.2 Develop chemical consumption minimised process for toxic metal removal ... 17  
      2.1.3 Determine the effect of the metal removal process on overall sludge characteristics ..... 18  
      2.1.4 Study the economic feasibility of the proposed sludge treatment process ....... 18  
   2.2 Research approach ................................................................................................. 19  
      2.2.1 Toxic metal removal ......................................................................................... 19  
      2.2.2 Effects on other sludge characteristics ............................................................ 20  
      2.2.3 Cost analysis .................................................................................................... 20  
3. Enhancing toxic metal removal from acidified sludge with nitrite addition ............... 22  
   Abstract ........................................................................................................................ 22
3.1 Introduction ................................................................................................................................. 23
3.2 Materials and methods .............................................................................................................. 23
  3.2.1 Sludge source ....................................................................................................................... 23
  3.2.2 Toxic metal solubilisation from acidified sludge ................................................................. 24
  3.2.3 Metal distribution analysis .................................................................................................. 24
  By analysing the concentration of metals in the residues of each extracting steps and calculating metals in each fraction by subtraction, the possible carryover of extracting solutions in each step could be minimised ...................................................................................................................... 26
  3.2.4 Effect of exposure time on metal removal ............................................................................ 26
  3.2.5 Effect of nitrite concentration on metal removal ................................................................. 26
  3.2.6 Analysis and calculation ...................................................................................................... 26
3.3 Results ........................................................................................................................................ 28
  3.3.1 Effect of nitrite addition on metal removal and distribution ............................................... 29
  3.3.2 Effect of nitrite exposure time and nitrite concentration .................................................... 31
3.4 Discussion .................................................................................................................................. 33
  3.4.1 Improvement to metal removal by nitrite ........................................................................... 33
  3.4.2 Practical implications ........................................................................................................... 34
3.5 Conclusions ............................................................................................................................... 36
4. In situ acidification and alkali production by an electrochemical system for toxic metal removal from sludge ......................................................................................................................... 37
Abstract ........................................................................................................................................... 37
4.1 Introduction ............................................................................................................................... 38
4.2 Materials and methods .............................................................................................................. 39
  4.2.1 Sludge source ....................................................................................................................... 39
  4.2.2 Electrochemical system and operation .................................................................................. 39
  4.2.3 Sludge treatment .................................................................................................................. 41
  4.2.4 Analytical methods and calculations .................................................................................... 41
4.3 Results and discussion .............................................................................................................. 42
  4.3.1 Sludge acidification and ES performance ............................................................................. 42
  4.3.2 Metal solubilisation ............................................................................................................. 44
4.3.3 Metal precipitation in the cathode compartment ........................................... 46
4.4 Conclusions ........................................................................................................... 47

5. Acidification with nitrite addition significantly improves sludge digestibility, dewaterability and pathogen reduction ........................................................................................................... 48
Abstract .................................................................................................................... 48
5.1 Introduction ............................................................................................................ 49

5.2 Materials and methods ......................................................................................... 50
  5.2.1 Sludge source ................................................................................................. 50
  5.2.2 Sludge treatment ............................................................................................ 50
  5.2.3 Digestibility ..................................................................................................... 51
  5.2.4 Dewaterability ............................................................................................... 53
  5.2.5 Pathogen concentration .................................................................................. 53
  5.2.6 Analysis and calculation .................................................................................. 53

5.3 Results and discussion ......................................................................................... 54
  5.3.1 Enhancement on sludge digestibility ............................................................... 54
  5.3.2 Enhancement on sludge dewaterability ............................................................ 58
  5.3.3 Effects on sludge pathogen concentration ....................................................... 59

5.4 Conclusions ......................................................................................................... 61

6. Electrochemical treatment to improve characteristics of primary sludge ............... 62
Abstract ..................................................................................................................... 62
6.1 Introduction .......................................................................................................... 63

6.2 Materials and methods ......................................................................................... 63
  6.2.1 Sludge source .................................................................................................. 63
  6.2.2 Sludge treatment ............................................................................................ 64
  6.2.3 Analysis of the PS characteristics .................................................................. 65
  6.2.4 Analytical methods and calculations ............................................................... 66

6.3 Results and discussion ......................................................................................... 66
  6.3.1 Metal removal ................................................................................................. 66
  6.3.2 Sludge dewaterability ..................................................................................... 68
6.3.3 Sludge digestibility ................................................................. 69
6.4 Conclusions ............................................................................. 71

7. Implications for practice ............................................................ 72

7.1 Introduction ............................................................................. 72
7.2 Material and methods ............................................................... 72
7.2.1 Costs for the treatment processes ......................................... 72
7.2.2 Benefits calculation .............................................................. 73

7.3 Results and discussion ............................................................. 75
7.3.1 Costs for the treatment processes ......................................... 75
7.3.2 Benefits from sludge treatment ............................................ 78

7.4 Conclusions ............................................................................. 85

8. Conclusions and recommendations ............................................ 86

8.1 Conclusions ............................................................................. 86
8.1.1 Toxic metal removal ............................................................. 86
8.1.2 Enhancement of sludge digestibility ....................................... 86
8.1.3 Enhancement of sludge dewaterability .................................... 87
8.1.4 Pathogen reduction ............................................................... 87
8.1.5 Economic analysis ............................................................... 87

8.2 Significance and implications of the research findings ................ 88

8.3 Recommendations for future studies ........................................ 90
8.3.1 Move to practical application ............................................... 90
8.3.2 Reveal of the working mechanism of nitrite and anodic process on sludge .................................................. 91

References ..................................................................................... 92
List of figures

Figure 1-1. Typical flowsheet of a WWTP with activated sludge process ........................................3

Figure 1-2. Sludge end use in Australia at 2013 ..............................................................................4

Figure 1-3 Schematic diagram of AD process ..................................................................................10

Figure 3-1. The change of distribution of metals in sludges from all 3 WWTPs after 24 hours of treatment with acidification and acidification + nitrite addition. (A) for Cu and (B) for Zn. Raw: control group without any treatment. pH2: sludge was maintained at pH 2.0 for 24 h. pH2 + nitrite: sludge was maintained for 24 h at pH 2.0 with a nitrite concentration of 20 mg NO₂⁻-N/L. Error bars show standard deviation from triplicate tests ....................................................................................................................31

Figure 3-2. The Cu and Zn removal efficiencies varying with treatment duration (0.5 - 24 h). The sludge treatment was conducted at pH 2.0 with nitrite addition at 20 mg NO₂⁻-N/L. .... 32

Figure 3-3. Effect of NO₂⁻-N concentrations on Cu and Zn removal efficiencies. The treatment was conducted at pH 2.0 for 24 hours. .................................................................................................................................32

Figure 4-1. Schematic diagram of electrochemical system for metal removal from sludge..............40

Figure 4-2. pH of sludge in the anode compartment during ES operation ........................................43

Figure 4-3. The electrode potential and cell voltage during the operation of ES. Error bars show the standard deviation. .................................................................................................................................43

Figure 4-4. Metal solubilisation for Cu (A) and Zn (B) after different treatments. Error bars show the standard deviation from triplicate solubilisation experiments. ........................................45

Figure 4-5. Metal concentration in aqueous phase (dots and solid lines) and pH change (dash lines) with time in cathode compartment ........................................................................................................46

Figure 5-1. Cumulative methane production from WAS exposed to different treatment. Error bars show standard deviation from triplicate tests. The symbols represent the measured data and the lines represent the model fit. ................................................................................................................55
Figure 5-2. Estimated biochemical methane potential ($B_0$) of WAS from different treatment. Error bars show 95% confidence intervals. .................................................................57

Figure 5-3. Solids content of belt filter dewatered sludge from different treatment..........................59

Figure 5-4. Concentration of total coliforms and E.coli in sludge after different treatment..........60

Figure 6-1. Removal efficiency of Cu (A) and Zn (B) after different treatment .........................67

Figure 6-2. Dewatered sludge cake solids content with different treatment............................69

Figure 6-3. Cumulative methane production from PS exposed to different treatments. Error bars show standard deviation from triplicate tests. The symbols represent the measured data and the lines represent the model fit. ........................................................................70

Figure 7-1 The cumulative cost for different sludge treatment over 25 years..........................80

Figure 7-2 Saving from treatment with disposal price change ..................................................81

Figure 7-3 The cumulative net benefit from sludge after different treatment...........................84

Figure 7-4 Additional benefits from ES treatment with different HRT of AD and solids content of dewatered sludge.................................................................85
List of tables

Table 1-1. Threshold of metal concentrations in some guidelines .............................................. 5
Table 1-2. Allowable land application for sludge of different grade ........................................... 5
Table 1-3. Effects of different pretreatment methods to improve AD of sludge ................................. 12
Table 3-1. SCE procedures ........................................................................................................ 24
Table 3-2. Sludge contaminant concentration values and biosolids grading thresholds .................... 28
Table 3-3. Toxic metal solubilisation from sludge (with standard deviation from triplicate tests) ........ 29
Table 3-4. Chemical cost for nitrite-based sludge treatment ......................................................... 34
Table 4-1. Concentration of toxic metals in WAS ........................................................................ 39
Table 5-1. Sludge solubilisation after different treatment, VS destruction and estimated hydrolysis rate coefficient for BMP tests ................................................................................. 56
Table 6-1. Concentrations of toxic metals in PS .......................................................................... 64
Table 6-2. SCOD of PS after different treatment and estimated hydrolysis rate coefficient (k) and biochemical methane potential (B_{0}) of the AD process ................................................................. 70
Table 7-1 Capital cost for sludge treatment systems .................................................................. 76
Table 7-2 The annual cost for HCl treatment ................................................................................ 77
Table 7-3 The annual cost for treatment of ES acidification + metal removal ................................. 78
Table 7-4 Annual cost of direct sludge disposal without AD ......................................................... 79
Table 7-5 Annual cost for sludge disposal after AD .................................................................... 82
Table 7-6 Power generation from AD of sludge after different treatment .................................... 83
# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>Anaerobic digestion</td>
</tr>
<tr>
<td>AEM</td>
<td>Anion exchange membrane</td>
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<tr>
<td>ASP</td>
<td>Activated sludge process</td>
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<tr>
<td>AUD</td>
<td>Australian dollar</td>
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<tr>
<td>BCR</td>
<td>Community Bureau of Reference</td>
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<tr>
<td>BDL</td>
<td>Below detection limit</td>
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<tr>
<td>BMP</td>
<td>Biochemical methane potential</td>
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<tr>
<td>CE</td>
<td>Current efficiency</td>
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<tr>
<td>CEC</td>
<td>Commission of the European Communities</td>
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<tr>
<td>CEM</td>
<td>Cation exchange membrane</td>
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<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
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<tr>
<td>DS</td>
<td>Dry solids</td>
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<tr>
<td>EBPR</td>
<td>Enhanced biological phosphorus removal</td>
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<tr>
<td>EPA</td>
<td>Environmental protection agency</td>
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<tr>
<td>EPS</td>
<td>Extracellular polymeric substance</td>
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<tr>
<td>ES</td>
<td>Electrochemical system</td>
</tr>
<tr>
<td>FNA</td>
<td>Free nitrous acid</td>
</tr>
<tr>
<td>HRT</td>
<td>Hydraulic retention time</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>MPN</td>
<td>Most probable number</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>MWS</td>
<td>Municipal wastewater sludge</td>
</tr>
<tr>
<td>NSW</td>
<td>New South Wales</td>
</tr>
<tr>
<td>p.a.</td>
<td>Per annum</td>
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<tr>
<td>PAO</td>
<td>Aoly-phosphate accumulating organism</td>
</tr>
<tr>
<td>PE</td>
<td>Population equivalent</td>
</tr>
<tr>
<td>PHA</td>
<td>poly-hydroxyalkanoate</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PS</td>
<td>Primary sludge</td>
</tr>
<tr>
<td>RE</td>
<td>Removal efficiency</td>
</tr>
<tr>
<td>SBR</td>
<td>Sequencing batch reactor</td>
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SCE  Sequential chemical extraction
SCOD  Soluble chemical oxygen demand
SHE  Standard hydrogen electrode
TCOD  Total chemical oxygen demand
TPAD  Temperature phased anaerobic digestion
TS  Total solids
TSS  Total suspended solids
TWAS  thickened waste activated sludge
VS  Volatile solids
WAS  Waste activated sludge
WWTP  Wastewater treatment plant
1. Introduction and literature review

This chapter introduces the aim for the study in this thesis and reviews the relevant literature. It presents the background of sludge management for wastewater treatment plants (WWTPs) and the demand for sludge treatment to reduce the cost for sludge disposal. The application on agricultural land is one important way for beneficial sludge reuse but it is limited by the contaminant contents, especially toxic metals and pathogens. The sludge treatment technologies attempting to reduce the sludge mass and volume, and remove contaminants from sludge were reviewed, especially approaches related to free nitrous acid (FNA) and electrochemical applications.

1.1 Introduction

The activated sludge process (ASP) is widely applied for biological treatment of municipal wastewater. But the enormous sludge production has become an environmental burden. The management of sludge, including conditioning, thickening, stabilisation, dewatering, drying and disposal, is typically contributing 30 - 50% (even up to 65%) of the cost for operating a WWTP (Pérez-Elvira et al., 2006). The disposal of sludge, especially by incineration or landfilling, also consumes considerable resources and introduces negative effects to the environment. Being rich in nitrogen (N), phosphorus (P) and organics, wastewater sludge (or also termed biosolids) is potentially a good resource for nutrient and energy recovery. Application of sludge on agricultural land as fertilizer or soil amendment material provides an opportunity of beneficial sludge reuse (Lu et al., 2012, Pritchard et al., 2010). However, due to the contaminant contents, such as toxic metals and pathogens, land application of sludge is usually stringently regulated to avoid possible damage or hazards to both environment and human health. Australia, Europe, and USA have all developed and adopted guidelines for the land application of sludge (C.E.C., 1986, NSW-EPA, 2000, USEPA, 1992).

Toxic metals, or so-called “heavy metals” including Cd, Cr, Cu, Ni, Pb and Zn, are removed from wastewater and accumulate in sludge during the wastewater treatment process. The concentration of toxic metals is a major criterion determining the suitability and the allowed application amount of sludge on agricultural land. Toxic metals can be removed from sludge by solubilisation (leaching) followed by solid/liquid separation. Chemical leaching by acid and bioleaching by microbial acid generation have been studied to solubilise metals from sludge for many years. However, the removal performance and cost efficiency of both methods are still not sufficient for widespread
practical applications. Therefore, there is a clear demand for improving the efficiency of metal removal from sludge.

Sludge contains a large number of pathogens which could be a huge potential biohazard if they are released to the environment without regulation. As a result, sludge is required to be stabilised to reduce the pathogen concentration before land application or disposal. Anaerobic digestion (AD) has been favoured as a sludge stabilisation technology because of much lower chemical or energy consumption than chemical/physical stabilisation and the simultaneously produced biogas (mainly CH₄ and CO₂) and sludge reduction achieved. However, the limited digestibility of waste activated sludge (WAS), with a typical digestible extent around 30% to 50% (Appels et al., 2008), results in low solids destruction and low biogas production from conventional AD. This limits the application of AD in small to medium scale WWTPs where AD cannot be self-sustaining by producing enough methane for heat and energy generation. Even in large WWTPs, enhancing the digestibility of the sludge in the AD process would be highly valuable due to the increased energy recovery and reduced disposal volumes. Hence, there are advantages in studying and improving the sludge treatment to increase sludge digestibility and develop alternative sludge stabilisation technologies.

For most sludge disposal routes, the total (wet) mass or volume of sludge is of major importance due to transportation costs or energy needs for incineration. Therefore sludge dewatering is a crucial step to minimise the amount of wet sludge. Typically, the dewatering process can achieve a solids content of around 15% - 30% (Wang et al., 2008). Many sludge treatment methods focus on improved sludge dewaterability, including chemical additions or physical methods.

To address the above challenges, sludge treatment has demanded great attention and interest of scientists and engineers. To develop effective and practical technology solutions for sludge treatment, a critical balance between the costs and benefits introduced by the treatment processes needs to be achieved. The aim of the work in this thesis is to develop and investigate a novel, more cost-effective technology that can address several challenges for sludge management, including removal of toxic metals and pathogens, as well as improving digestibility and dewaterability.
1.2 Literature review

1.2.1 Sludge production, reuse and regulation

A wastewater treatment plant (WWTP) with activated sludge process (ASP) usually includes primary sedimentation, activated sludge treatment tank, secondary sedimentation and optional anaerobic digestion, as briefly illustrated in Figure 1-1. The sludge is mainly harvested from primary and secondary clarifiers, namely primary sludge (PS) and waste activated sludge (WAS), respectively. If the sludge is treated (such as anaerobic digestion) to a standard acceptable level and ready for beneficial reuse, it will be defined as biosolids. Due to wide and increasing application of ASPs, the sludge (or biosolids) production worldwide is enormous. In Australia, the biosolids production is about 330,000 tonnes of dry solids per year (ANZBP, 2013). The wastewater solids production was over 6.5 million tonnes in 2004 in America (IWA-WaterWiki, 2013). The European Union (EU) produces about 10 million tonnes of dry sludge annually (Grøn, 2007). It was estimated the sludge production per capita per day was about 65 - 100 g of dry solids (Hudson, 1995).

![Figure 1-1. Typical flowsheet of a WWTP with activated sludge process](image)

The considerable amount of sludge production creates a huge burden for the WWTP operators for sludge management, especially for end disposal. Landfilling is one conventional method for sludge disposal. But the decreasing land availability and the problems from greenhouse gas emission and leachate make it more and more difficult and expensive (Wang et al., 2008). Incineration can significantly reduce the volume of sludge/ash for disposal. But sludge usually has a high water
content and requires drying before incineration, which introduces extra demands for handling and significant energy consumption. The gas emission and the disposal of ash from incineration add further difficulties to the process and make it more expensive. Beneficial reuse of sludge in agriculture as fertilizer or soil amendment material is considered as a sustainable method for sludge end use (Lu et al., 2012, Pritchard et al., 2010). Figure 1-2 presents the end use of sludge in Australia in 2013 (ANZBP, 2013). Including agriculture, land rehabilitation and landscaping, about 70% of all sludge produced was used beneficially on land.

![Figure 1-2. Sludge end use in Australia at 2013](image)

Apart from the organic matter and nutrients, contaminants are also removed from wastewater and accumulate in the sludge stream during the ASP, especially toxic metals including Cd, Cr, Cu, Ni, Pb and Zn. The presence of toxic metals often limits the opportunities for land application (Smith, 2009). To avoid long-term environmental problems, the regulation of land application of sludge is strictly based on the relevant policies or guidelines. For example, the U.S. Environmental Protection Agency (USEPA) has specified the “ceiling concentration” and limited cumulative pollutant loading rate for the sewage sludge application on agricultural land (USEPA, 1992). The Commission of the European Communities (C.E.C.) Directive also sets the limit of heavy metal concentrations in sludge for agricultural use and the amounts of heavy metals added annually to agricultural land (C.E.C., 1986). In Australia, sludge is classified into different grades according to the concentrations of toxic metals (and some chemicals), which determine the sludge reuse options. A maximum allowable biosolids application rate is also set for agricultural application (NSW-EPA, 2000). The threshold of metal concentrations for land application in those guidelines is presented in
Table 1-1. In Australia, the allowed land application options of sludge in different grades are presented in Table 1-2.

**Table 1-1.** Threshold of metal concentrations in some guidelines

<table>
<thead>
<tr>
<th>Sludge reuse guidelines</th>
<th>Concentrations (mg/kg dry solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Australia</td>
<td></td>
</tr>
<tr>
<td>Grade A</td>
<td>3</td>
</tr>
<tr>
<td>Grade B</td>
<td>5</td>
</tr>
<tr>
<td>NSW-EPA</td>
<td></td>
</tr>
<tr>
<td>Grade C</td>
<td>20</td>
</tr>
<tr>
<td>Grade D</td>
<td>32</td>
</tr>
<tr>
<td>C.E.C. Directive limit values</td>
<td>20 - 40</td>
</tr>
<tr>
<td>USEPA ceiling concentrations</td>
<td>85</td>
</tr>
</tbody>
</table>

**Table 1-2.** Allowable land application for sludge of different grade

<table>
<thead>
<tr>
<th>Allowable land application use</th>
<th>Grade A</th>
<th>Grade B</th>
<th>Grade C</th>
<th>Grade D</th>
<th>Grade E*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Home lawns and gardens</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Public contact sites</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Urban landscaping</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Agriculture</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Forestry</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>×</td>
</tr>
<tr>
<td>Soil and site rehabilitation</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>×</td>
</tr>
<tr>
<td>Landfill disposal</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Surface land disposal</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
</tbody>
</table>

* Grade E stands for those sludge within which the metal concentrations exceed contaminant acceptance concentration for Grade D in Table 1-1

Besides toxic metals, pathogen contents in sludge are another concern requiring attention before land application of sludge. As such, sludge stabilisation is required to reduce the pathogen concentration prior to land application. The sludge is divided into different stabilisation categories.
based on the stabilisation treatment it has gone through or the concentration of certain pathogen indicator(s) in sludge.

To maximise the opportunities of land application and reduce the costs for sludge disposal or reuse, many studies have been focusing on sludge treatment to remove metal and pathogen contaminant(s).

1.2.2 Toxic metals removal from sludge

1.2.2.1 The presence of toxic metals in sludge

Toxic metals usually are removed from wastewater and fixed into sludge during ASP. The total content of toxic metals in sludge could take up to 0.5 - 2.0% on a dry weight basis (Babel and del Mundo Dacera, 2006). The recognition of metal distribution in sludge can provide helpful information for metal removal. The amount and distribution of metals can vary markedly depending on the source water quality, the sludge characteristic and the chemical properties of the metals. Sequential chemical extraction (SCE) is widely used to determine the chemical distribution of metals in sludge. With a series of chemical agents extracting in a specific sequence, metals in different forms will be solubilised step by step (Marchloretto et al., 2002). There are several SCE procedures to fractionate metals in sludge samples using different extracting agents, which separate metals into various fractions (Filgueiras et al., 2002, Lake et al., 1984, Sims and Kline, 1991, Tessier et al., 1979, Ure et al., 1993). Commonly, the metals in sludge can be characterised as the following types: soluble; exchangeable (adsorbed onto organic/biological or inorganic compounds); organically bound; inorganically bound (precipitated with sulfide, hydroxide, carbonate etc.); and residues. It should be noted that SCE does have pitfalls when being used for metal distribution analysis (Nirel and Morel, 1990). However, the step by step extraction adopted in the SEC procedures is capable of distinguishing metals combined with different compounds in solids and providing “operationally defined” information about the metal distribution (Tessier et al., 1979).

For most of the metals, the organically bound fraction usually makes up a fairly large component (Babel and del Mundo Dacera, 2006, Daskalakis et al., 2013, Lake et al., 1984, Marchioletto, 2003, Wang et al., 2005), which agrees with the fact that extracellular polymeric substances (EPS) are an important sink for toxic metals in sludge (Brown and Lester, 1979, Liu et al., 2001, Tian et al., 2006). Another important metal fraction is the inorganically bound, particularly sulfide and carbonate precipitates. Knowing the forms of metals present in sludge, several methods can be adopted to remove these metals from sludge, mainly by metal solubilisation followed by
solid/liquid separation and precipitation from the liquid phase. Thereby, metal solubilisation or leaching becomes the most critical step for metal removal.

1.2.2.2 Toxic metal removal by chemical leaching

A variety of acids have been employed for solubilising metals from sludge. Veeken and Hamelers (1999) found that the performance of leaching Cu and Zn with organic acids was better than using nitric acid due to the complexing capacity of organic acids. The best metal removal process achieved about 80% Cu and 100% Zn solubilisation with citric acid at pH 1.5. Marchioretto (2003) investigate the acid leaching efficiency of organic acids and inorganic acids. The results showed that at pH 3 and pH 4, citric acid had the best metal leaching performance, which is again likely caused by the complexing properties of citrate anion. When the pH value was lower than 2, nitric acid (HNO₃) and hydrochloric acid (HCl) achieved similar metal extraction efficiencies. The leaching of Cu was difficult, with the best extraction efficiency reaching only 40% at pH 1, which was believed due to the fact that Cu was predominantly bound to the organic fraction. Daskalakis et al. (2013) used 10% H₂SO₄ (v/v) to remove metals from activated sludge from a membrane bioreactor, achieving removal of 78% Zn and 47% Cu. They also revealed that about 41% of Cu was bound to organics and sulfide, which could be the reason for the limited removal. Similarly, the difficulty of removing Cu from sludge has been reported in many other studies using acid leaching (Babel and del Mundo Dacera, 2006, Lo and Chen, 1990, Logan and Feltz, 1985). The main reason reported for the poor leaching of Cu is that Cu is mostly bound to organics and sulfide, which are relatively resistant to acid leaching.

To improve the metal removal from sludge, advanced oxidation was proposed and studied with the aim to release metals bound with organics. Yoshizaki et al. (2000) found that with a 2% H₂O₂ addition, the removal of Cu by phosphoric acid (H₃PO₄) was increased from 9% to 92%. In a pilot-scale study of peroxidation of sludge, Neyens et al. (2003) found that the treatment at pH 3 with Fe²⁺ and H₂O₂ addition (Fenton reagents) could increase the solubilised fraction of Cu from 0.019 mg/l to 1.33 mg/L. In the same study, they concluded that peroxidation degraded the EPS in the sludge and enhanced the sludge dewaterability. The degradation of EPS could also be the reason for the improved Cu solubilisation as EPS is a main sink for bound metals. Similarly, Dewil et al. (2006) used Fenton peroxidation to treat sludge and achieved more than 50% of Cu concentration reduction in the final sludge solids. Some physical processes were also studied to assist the acid extraction of toxic metals from sludge. Deng et al. (2009) found that with 20 min of ultrasound assisting 0.325 M HNO₃ extraction, the removal of Zn and Pb from sludge were higher than 80%
but only 9.5% of Cu could be extracted. Arain et al. (2008) used microwave and ultrasound to assist metal extraction from sludge. They found that each step of sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) could be reduced from 16 h to 15 - 30 min or 60 - 120 s with the assistance of ultrasound or microwave, respectively, while still achieving similar extraction efficiency.

1.2.2.3 Toxic metal removal by bioleaching

Bioleaching is the process of microbial oxidation of insoluble metal sulfides and the solubilisation of metal ions, which can happen through direct or indirect mechanisms. In the case of direct bioleaching, sulfide/sulfur oxidizing bacteria gain electrons directly from sulfide. Simultaneously, the metal will be released to the solution in the form of ions (Isamu, 2001). However, many discussions and studies showed that the indirect mechanism played the dominant role in bioleaching (Mishra et al., 2005, Rohwerder et al., 2003, Tributsch, 2001), as described by equation 1-1, 1-2 and 1-3 (M stands for divalent metals):

\[
MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S^0 \quad (1-1)
\]

\[
4Fe^{2+} + O_2 + 4H^+ \xrightarrow{Bacteria} 2H_2O + 4Fe^{3+} \quad (1-2)
\]

\[
2S^0 + 3O_2 + 2H_2O \xrightarrow{Bacteria} 4H^+ + 2SO_4^{2-} \quad (1-3)
\]

Metal sulfide is an important form of toxic metals present in sludge and acidification is necessary for metal solubilisation since many metals would precipitate as metal hydroxides at pH values above 3. As a result, bioleaching has been used for removal or recovery of metals from waste. Acidithiobacillus ferrooxidans was reported for its application of leaching metals from dewatered sludge. After 40 days treatment, the solubilisation efficiencies of Zn, Cu and Cr were 42%, 39% and 10%, respectively. It was found that the high sludge concentration inhibited the leaching rate due to the high buffering capacity, which made it difficult to achieve and maintain a low pH (Kim et al., 2005). In a continuous system, acidophilic Acidithiobacillus sp. was employed with sulfur powder for solubilising metals in anaerobically digested municipal sludge. Using a hydraulic retention time (HRT) of 14 days, the solubilisation efficiencies of Cd, Cu, Ni and Zn were 50%, 33%, 48% and 74%, respectively. Increasing the sulfur concentration and the HRT could improve the metal leaching process while the addition of ferrous ions did not have much effect on performance (Seth et al., 2006). Peng et al. (2011) integrated bioleaching and electrokinetic remediation to solubilise
and remove metal from sludge. The whole treatment lasted 10 days (6 days of bioleaching and 4 days of electrokinetic remediation). The pH in the bioleaching compartment was driven from 6 down to 2.8. The removal efficiencies of Cu and Zn were 88% and 98%, respectively.

Bioleaching is a complex multi-step process with a combination of biological and chemical reactions. The metal removal efficiency is affected by many factors. It was found that pre-acidification and low initial pH led to higher metal solubilisation (Blais et al., 1993, Pathak et al., 2009). Sreekrishnan (1993) found that the lower initial pH increased acid production and metal solubilisation rates. It is still an open question if pre-acidification is a good way to start bioleaching for sludge, considering the costs associated with the acid addition process. Other parameters affecting bioleaching performance are energy resource (sulfur or ferrous), microorganism species, solid and organic content in the sludge (Chan et al., 2003, Fang and Zhou, 2007, Lombardi et al., 2001).

1.2.2.4 Difficulties with metal removal from sludge

Based on the above review of metal removal processes from sludge by chemical leaching and bioleaching, the advantages and disadvantages for both of these two technologies can be considered. Chemical leaching, especially acid leaching, can accomplish satisfactory removal for most toxic metals in less than 1 d of reaction. But the acid consumption of obtaining acidic conditions lower than pH 2 and the insufficient removal for organically bound metals, such as Cu, limit its practical application. Advanced oxidation can significantly enhance the metal removal efficiency of organically bound metals. But the requirement of ferrous salts and H₂O₂ also dramatically increase the costs. A more cost-effective way to improve the metal removal by acid leaching would be of great interest generally. Bioleaching has the potential of reducing or avoiding the chemical consumption thus reduce the cost for metal removal from sludge. However, the long HRTs (typically longer than 10 d) required for the bioleaching process increase the capital investments due to the large reactor size. In addition, the requirement for aeration, sulfur and ferrous salt additions make bioleaching not a chemical/energy free process and can actually generate considerable operating costs. Therefore, further investigations into both acid leaching and bioleaching for metal removal from sludge are necessary and both of these two technologies will have potential for practical applications, depending on the conditions in each individual case, such as the availability and costs of space as well as other resources, such as energy and chemicals.
1.2.3 Anaerobic digestion of sludge

1.2.3.1 Process and limitation of anaerobic digestion

Anaerobic digestion (AD) is a favoured and widely applied technology for sludge stabilisation and reduction (Appels et al., 2008). The process of AD is that certain types of microorganisms convert the (bio)degradable organic matter in sludge into biogas (mainly methane and carbon dioxide) under anaerobic conditions, achieving sludge reduction and energy recovery. Additionally, the concentration of pathogens is also reduced at the same time. The entire AD process includes four interdependent steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis, as shown in Figure 1-3.

![Figure 1-3 Schematic diagram of AD process](image)

Two critical parameters characterising the AD performance of sludge are degradation rate and extent. Degradation rate describes how fast the sludge can be digested and therefore determines the hydraulic retention time (HRT) for the AD process. Sludge with a higher degradation rate requires shorter HRT for similar solids degradation, which consequently reduces the volume of digestion reactors. The degradation extent represents the maximal fraction of sludge that can be digested, determining the ultimate biogas production and sludge reduction through AD. The limitation from both of these two parameters constrains the application of AD for sludge.

Conventional AD of sludge usually has an HRT of 15 - 30 days during which the overall extent of degradation is only up to 30 - 50% (Appels et al., 2008). Primary sludge is readily digestible due to its large fraction of easily degradable carbohydrates, proteins and lipids from raw sewage (Gavala et al., 2003). But the digestibility of waste activated sludge is relatively poor, with
hydrolysis being generally recognised as the rate limiting step (Carrère et al., 2010). EPS plays an important role in forming the microbial matrix in activated sludge and makes up a significant fraction in waste activated sludge (Bura et al., 1998). But EPS is also known to be relatively recalcitrant to AD processes (Carrère et al., 2010), limiting the digestibility of WAS.

1.2.3.2 Pretreatment to increase digestibility

A wide range of pretreatment options have been studied to increase the digestibility of sludge, especially for waste activated sludge. Both degradation rate and extent are targeted for improvement to increase biogas production and decrease the HRT required for AD.

Thermal pretreatment employs heat (usually 150 - 200 °C) for about 30 - 60 min to enhance sludge hydrolysis and solubilisation and thus increases the digestibility of sludge. It was found that sludge solubilisation and biodegradability increased with the pretreatment temperature (Carrère et al., 2008). But when the temperature was higher than 170 °C, the Maillard reaction would cause the formation of recalcitrant compounds, which could reduce sludge degradability (Carrère et al., 2010, Pinnekamp, 1989) and increases the soluble colour concentration in the AD effluent. Ultrasonic treatment is also able to cause disruption of sludge flocs and sludge solubilisation, which consequentially improves the sludge digestibility (Bougrier et al., 2005).

Sludge solubilisation and disintegration can also be achieved by many chemical agents, hence chemical pretreatment is effective for digestibility enhancement. Alkali compounds, such as NaOH and KOH, are used to raise the sludge pH for pretreatment and improve the AD of sludge (Zhang et al., 2010). Alkali treatment often combines with thermal treatment to achieve a better and faster sludge solubilisation and anaerobic digestion (Valo et al., 2004, Vlyssides and Karlis, 2004). In addition, strong oxidizing agents, such as ozone and hydrogen peroxide, are used to improve the AD of sludge in many studies (Carrère et al., 2010).

Temperature phased anaerobic digestion (TPAD) is another technology to improve AD of sludge. Using an extra biological stage at 55 - 70 °C before mesophilic (30-35°C) AD, TPAD enhances the sludge hydrolysis. The TPAD process has a strong effect on improving the degradation rate but has only a limited effect on the extent of degradation (Batstone et al., 2011).

Several studies regarding pretreatment for enhancing AD of sludge are summarised in Table 1-3.
**Table 1-3.** Effects of different pretreatment methods to improve AD of sludge

<table>
<thead>
<tr>
<th>Pretreatment condition</th>
<th>Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>170 °C, 7 bar for 30 min</td>
<td>CH$_4$ production increased for about 48 - 55%</td>
<td>Fdz-Polanco <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>175 °C, for 40 min, 2.9 d AD of centrate after sludge treatment and centrifuge</td>
<td>Solubilised 16% of TSS during the thermal treatment; 65% reduction of TSS overall</td>
<td>Graja <em>et al.</em> (2005)</td>
</tr>
<tr>
<td>Compare 130 °C + pH 10 vs. 150 °C vs. 170 °C, all the treatment lasted for 30 min</td>
<td>Solubilised 49 - 57% of TCOD, roughly 80% CH$_4$ yield increase</td>
<td>Bougrier <em>et al.</em> (2006)</td>
</tr>
<tr>
<td>70 - 210 °C for 30 min</td>
<td>Up to 80% of insoluble COD was solubilised. Biodegradability and CH$_4$ production were increased by 23 - 78%.</td>
<td>Carrère <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>20 kHZ, specific energy for treatment ranged from 0 to 15,000 kJ/kg TS</td>
<td>Up to 28% of TCOD was solubilised; biogas production was increased by 25-140%</td>
<td>Bougrier <em>et al.</em> (2005)</td>
</tr>
<tr>
<td>pH 10 for 8 days</td>
<td>CH$_4$ production was increased by 340%; SCOD was increased from 62 m g/L to 11800 mg/L</td>
<td>Zhang <em>et al.</em> (2010)</td>
</tr>
<tr>
<td>pH 8 - pH 11, 50 - 90 °C for 10 h</td>
<td>SCOD was increased by up to 69000 mg/L, methane production was increased by about 150%</td>
<td>Vlyssides <em>et al.</em> (2004)</td>
</tr>
<tr>
<td>50 - 70 °C for 2 days</td>
<td>Sludge degradability was increased from 21% to 49% with temperature from 50 °C to 65 °C</td>
<td>Ge <em>et al.</em> (2011)</td>
</tr>
<tr>
<td>pH 10 - pH 12, 130 - 170 °C for 1 h</td>
<td>SCOD was increased for up to 83%, biogas production in continuous AD was improved by 54%</td>
<td>Valo <em>et al.</em> (2004)</td>
</tr>
</tbody>
</table>

Most of the pretreatment methods reviewed above require significant resource input, including chemicals, energy for heating, pumping and mixing as well as capital investments for extra equipment and reactors if required. The benefits of pretreatment come from the improved extent and rate of digestion. Higher digestion extent leads to a higher volatile solids (VS) destruction and
methane production, resulting in reduced sludge volume after digestion and more energy recovery from biogas. By increasing the digestion rate, a shorter HRT of the AD process can be achieved, which means the required reactor size may be reduced, making corresponding savings in capital investments. Alternatively, a higher VS destruction could be achieved for a given HRT, providing the same benefits as mentioned above.

To achieve major improvement for both digestion extent and rate, a high-intensity pretreatment is typically needed, *i.e.* using high energy and/or chemical inputs, such as for thermal hydrolysis. Relatively low-intensity pretreatments, *e.g.* mechanical or thermophilic biological processes, often only increase the digestion rate (Carrère *et al.*, 2010). Therefore, the net benefits in practical pretreatment applications for AD will very much depend on the balance between the value of energy/chemical inputs for the pretreatment and the extra benefits gained from improved sludge digestion such as increased biogas production, VS destruction and dewaterability.

1.2.4 Nitrite application in wastewater industry

Recently, nitrite has been recognised as a promising agent bringing multiple benefits in various wastewater treatment processes.

Zhou *et al.* (2007) found that nitrite, at a concentration ranging from 35.9 to 103.5 mg N/L, was able to inhibit the anoxic phosphorus (P) uptake in enhanced biological phosphorus removal (EBPR) systems. It was revealed that the formed free nitrous acid (FNA, *i.e.* HNO$_2$) was likely the actual inhibitor given the much stronger correlation of the P uptake rate with FNA concentration than nitrite concentration. Later, Pijuan *et al.* (2010) found that nitrite/FNA also had inhibitory effects on poly-hydroxyalkanoates (PHA) oxidation, phosphate uptake, glycogen replenishment and growth of poly-phosphate accumulating organisms (PAOs). It was noticed again that the inhibition was strongly associated with the FNA concentration rather than the nitrite concentration, hence FNA was likely the true inhibitor. They also found that FNA seemed to only inhibit the metabolism of PAOs rather than killing PAOs since the activity recovered within hours once the FNA was removed. It is worth noticing that all the above reported inhibition effects were caused by a FNA-N concentration in the µg/L range.

Jiang *et al.* (2011) found that FNA had strong biocidal effects on anaerobic sewer biofilms when the FNA-N concentration was increased to mg/L level. The viable fraction of microorganisms was decreased by 65 - 75% after treatment with FNA concentrations above 0.2 mg-N/L for 6-24 h. The FNA concentration had a strong correlation with the biocidal effect. It was also found that the
biocidal effects were reduced when the mass transfer was limited by a thick biofilm. Some microorganisms were relatively resistant to FNA, surviving at treatment up to 3 mg FNA-N/L for 24 h. In their later study, it was found that FNA and hydrogen peroxide had synergistic inactivation effects on anaerobic wastewater biofilms. At a concentration of 0.255 mg FNA-N/L and 10 - 150 mg H₂O₂/L for 6 h treatment, the inactivation efficiency was increased by about one log unit compared to the treatment with FNA alone (Jiang and Yuan, 2013).

When applied to sludge, FNA also showed the capacity to effectively kill cells. Pijuan et al. (2012) found that the treatment with an FNA concentration of 2.02 mg-N/L for 24 h killed about 80% of viable cells in sludge withdrawn from a denitrifying sequencing batch reactor (SBR). With a treatment of 48 h, the biomass activity was eliminated completely and did not recover at all within 72 h after the nitrite was removed. In the same study, the sludge degradability by aerobic digestion was observed to be substantially improved. Similarly, in a SBR treating synthetic domestic wastewater, half of the excess sludge was exposed to FNA treatment (at 2.0 mg-N/L for 24-42 h) and then returned to the parent reactor, the final sludge production from the SBR was reduced by 28% and the particle size of the sludge was also reduced by approximately 10% (Wang et al., 2013b). Wang et al. (2013a) also used FNA to treat real WAS to improve its degradability by AD. It was found that the treatment at FNA concentrations less than 2.13 mg-N/L for 24 h enhanced sludge solubilisation as indicated by the increased SCOD, soluble proteins and soluble polysaccharides. The methane production from 44 days AD of treated WAS was increased by up to 27%. Both of the hydrolysis rate (k) and biochemical methane potential (B₀) were estimated to be improved by fitting the experimental data to a first-order kinetic model. The combination of FNA and heat pretreatment was able to enhance the WAS digestibility by AD even further (Wang et al., 2014).

Nitrous acid is a weak acid with a pKₐ = 3.34 at 25 °C. For all the above studies concerning nitrite and FNA, the treatment was mostly conducted at near neutral pH (pH > 5). As a result, those studies used a nitrite concentration of a few hundred mg-N/L to achieve the desired FNA concentration of less than 5 mg-N/L. The pH plays an important role on the treatment effects by determining the FNA concentration. It was hypothesised that the possible EPS disruption caused by FNA was the main reason for the changes resulting from the FNA addition to the sludge treatment. Recently, Zhang et al. (2015) discovered that FNA directly affects EPS by specifically targeting protein-like substances and hence breaking down the macromolecules within the EPS matrix into smaller molecules. Considering the critical role of EPS in sludge (Tian et al., 2006, Wei et al., 2012), FNA has great potential to bring further benefits to sludge management. In addition, there is also interest
on studying the effects of different pH and nitrite combinations to determine the optimum conditions for sludge management.

1.2.5 Electrochemical system in wastewater industry

In an electrochemical system (ES), the oxidation process and the reduction process occur on the anode and cathode, respectively, with the ions and charges migration driven by the electric field. These processes can be employed to solve problems in wastewater or water treatment, including electrocoagulation, electrofloculation, electrochemical metal reduction (recovery or removal) (Chen, 2004).

Recently, it was found that the ES can be used to produce valuable chemicals that are commonly utilised in water or wastewater treatment. Rozendal et al. (2009) achieved a production of 1.9 kg H₂O₂/m³/d from the cathode of an ES. A microbial anode was adopted in an ES to oxidise acetate and provide most of the energy for the H₂O₂ production in the cathode, with an overall efficiency of 83.1%. As such, the external energy demand was only 0.93 kWh/kg H₂O₂, which was much lower than a conventional electrochemical production requiring 4.4 - 8.9 kWh/kg H₂O₂. Rabaey et al. (2010) used a litre scale ES with microbial anode oxidizing acetate and real wastewater from a local brewery and manage to generate a caustic solution up to 3.4 wt%. With their technology, the cost for producing low strength caustic was around $0.1 per kg. ES was proved to be able to generate caustic in situ from sewage for controlling sewer corrosion (Pikaar et al., 2011b). At an average cell voltage of 5.2 V for 4 h, the caustic production at the cathode generated a 0.61 wt% caustic solution. The electric efficiency was about 53% for the production of caustic. After this, Pikaar et al. (2012) claimed that the combination of the cathode caustic production and the anode oxygen generation could deactivate the biofilms and remove sulfide in sewer pipes and therefore represented an effective sewage corrosion control route. They also observed the accumulation of proton in the anode compartment when there was blockage happening for the anode compartment flow, indicating the acid generation from ES, which is well known and often a problem especially for bioelectrochemical systems (Arends and Verstraete, 2012).

Electrochemical systems have also been used for direct sludge treatment. Drogui et al. (2013) investigated an electrooxidation process for municipal wastewater sludge (MWS) stabilisation and conditioning. After conditioning with H₂SO₄ at pH 4 - 5, a cylindrical electrolytic cell with RuO₂ coated Ti anode and Ti cathode was used for electrooxidation at a current density of 4.71 A/dm² for 60 min. The ES treatment increased the solids content of sludge after dewatering to 33.4% from
23.9% of the untreated sludge. Pathogens were also killed during the ES treatment, indicated by the decrease of a generic indicator (total coliform) concentration by more than 5 log units. Yu et al. (2014) used a membrane-less ES with Ti/RuO₂ mesh plate as electrode for secondary sludge treatment. With the cell voltage controlled at 20 V for 40 min, as well as a sodium hypochlorite dosage of 0.6% (V/V), the biogas production from the treated sludge was increased by up to 63.4%. They found that the ES treatment resulted in a huge change in the molecular weight (MW) distribution, with the fraction with MW>20 kDa decreasing from 84.2% to 49.1%. The hypochlorite was thought to be the key agent causing the disintegration of sludge.

An ES can drive a variety of redox reactions by electricity input. It also has the capacity to produce commonly used chemical agents for sludge treatment, namely acid or alkali compounds. Given that sludge from WWTP is basically in the form of a slurry or liquid, there will be a great potential to use ES for sludge treatment to create a chemical-free process and achieve significant benefits for sludge management.

1.2.6 Knowledge gaps

Based on the above reviewed literature, the need for a more cost-effective and environmentally friendly technology for sludge treatment to promote beneficial sludge reuse is clearly identified. Major improvements that need to be targeted includes reduced toxic metal and pathogen concentrations, improved digestibility and dewaterability. It is also important to achieve these improvements with minimum chemical and energy inputs and short retention times to minimise capital costs.

As shown above, the addition of nitrite/FNA has the ability to change sludge characteristics, but how effective it would be at improving toxic metal removal has not been studied so far. Furthermore, the integration of nitrite/FNA treatment with an electrochemical system needs to be investigated for its ability to remove toxic metals and reduce treatment costs. The effect of the combined electrochemical and nitrite/FNA treatment on other mentioned sludge characteristics are at this stage unknown as well. Finally, the balance of benefits and costs introduced by the treatment needs to be evaluated also as an indicator of its potential for practical application.
2. Research objectives and thesis overview

In this chapter, research objectives and questions are developed according to the knowledge gaps identified in the literature review. The overall research approach is then proposed to answer the research questions and accomplish the research objectives. This also reflects the thesis structure and hence provides an overview of the thesis.

2.1 Research objectives and questions

The main aim of this thesis is to develop and investigate a novel sludge treatment technology that effectively integrates the benefits of nitrite/free nitrous acid (FNA) and electrochemical processes. The overarching objective is to create a technology that achieves multiple benefits for sludge management including enhanced toxic metal removal and pathogen reduction from sludge as well as improved sludge digestibility and dewaterability. This overall thesis objective is broken down into specific research objectives as outlined in the following sections.

2.1.1 Use nitrite to enhance toxic metal removal from sludge

Toxic metal removal from sludge is limited by the low removal efficiency, especially for metals bound with organics or extracellular polymeric substances (EPS). Nitrite/FNA has been found to be able to break down microbial flocs and EPS in sludge. The first research objective of this thesis is to determine the feasibility of using nitrite to enhance the acid leaching of toxic metals from sludge.

- Will nitrite addition to acidified sludge affect the toxic metal solubilisation, and to what extent?
- How will nitrite addition affect the metal distribution in sludge?
- What will be the optimum condition for using nitrite to assist metal removal from acidified sludge?
- How will nitrite addition change the economics for toxic metal removal from sludge?

2.1.2 Develop chemical consumption minimised process for toxic metal removal

For toxic metal removal from sludge, the need to purchase, transport, handle and store the corrosive chemicals, i.e. concentrated acid and alkali, generates considerable costs for the sludge management.
There are also significant operational requirements such as occupational health and safety (OH&S) considerations created by the use of these chemicals. The second research objective is therefore to develop a new technology to avoid the use of acid and alkali for toxic metal removal from sludge. An electrochemical system (ES) was selected in this thesis for the in situ sludge acidification and alkali production.

- How can the ES be best used to achieve sludge acidification for metal solubilisation and alkali production for metal removal/recovery?
- How will the electrochemical acidification affect the metal solubilisation efficiency, compared to acidification with direct acid dosing?
- How will nitrite addition to the ES acidified sludge affect the overall metal removal performance?

2.1.3 Determine the effect of the metal removal process on overall sludge characteristics

Other sludge characteristics, including digestibility, dewaterability and pathogen content, also play critical roles on determining the overall cost/benefit outcome for sludge management. The third research objective is to investigate the effects of the treatment process employed for metal removal on these important sludge characteristics.

- How will the sludge digestibility during anaerobic digestion (AD) be affected by the acidification and nitrite addition treatment used for metal removal? Will different acidification methods, i.e. by direct acid dosing or via an electrochemical system, have different effects on the sludge digestibility? Will the removal of toxic metals improve the AD of sludge?
- How will the acidification and nitrite addition treatment affect the sludge dewaterability?
- Will the acidification and nitrite addition treatment reduce the pathogen concentrations in the sludge?

2.1.4 Study the economic feasibility of the proposed sludge treatment process

The practical application of sludge treatment technology depends on the balance between the costs and benefits introduced by the treatment process. The last research objective of this thesis is to evaluate the economic feasibility of the newly developed sludge treatment technology.
• By achieving benefits of enhanced toxic metal removal, pathogen reduction, sludge digestibility and dewaterability, will the acidification with nitrite/FNA treatment bring a positive value for sludge management?

• How will different acidification methods, *i.e.* by HCl dosing or ES, affect the economic potential?

• Where do the benefits possibly come from?

2.2 Research approach

To answer the research questions and achieve the objectives, real sludge from local municipal wastewater treatment plants were collected and treated. The effects of the sludge treatment were investigated as follows:

2.2.1 Toxic metal removal

The waste activated sludge (WAS) was acidified to pH 2 by acid dosing and nitrite was introduced to the acidified WAS. The metal solubilisation efficiency was investigated after 24 h of treatment. To understand the change of sludge caused by the treatment, sequential chemical extraction was undertaken afterwards to analyse the metal distribution in the WAS. To optimise the process, the effect of exposure time and nitrite concentration on metal removal was evaluated. (Chapter 3)

To avoid the use of the external acid and alkali for the toxic metal removal from WAS, a three-compartment ES was configured for *in situ* sludge acidification and alkali production. During the operation of ES, the WAS was acidified in the anode compartment. Then the optimum condition of nitrite concentration and treatment duration determined in the previous step was adopted for toxic metal solubilisation. To integrate the overall treatment, solid/liquid separation was conducted and the liquor with solubilised metals was added into the cathode compartment of ES, where the metals were precipitated by the *in situ* alkali production. The solubilisation efficiency of direct acid dosing and ES acidification was compared and the metal removal efficiency in the cathode compartment was studied. (Chapter 4)
2.2.2 Effects on other sludge characteristics

Based on the outcomes from the previous steps, the optimised treatment conditions for toxic metal removal were determined. The effects of the same condition on other sludge characteristics, i.e. digestibility, dewaterability and pathogen content, were then evaluated. (Chapter 5)

- **Sludge digestibility**

After the treatment, the WAS digestibility by AD was evaluated by batch biochemical methane potential (BMP) tests. The apparent first order hydrolysis rate coefficient \((k)\) and biochemical methane potential \((B_0)\) were adopted as the key parameters for the assessment of the digestibility after different pretreatment methods. The values for them were estimated by fitting a first-order kinetic model to the BMP data.

- **Sludge dewaterability**

After the treatment, the WAS was dewatered by a belt filter proxy process. The total solids content of the dewatered WAS was used as the parameter representing the dewaterability to compare the effects of different treatment options.

- **Pathogen reduction**

Total coliform and *E.coli* were selected as the indicators of the pathogens in the WAS. The concentration of the indicators was tested by commercialised testing kit, Colilert-18 (IDEXX, U.S.A). The concentrations of the indicators were compared to evaluate the microbial stabilisation effect of different treatment methods.

Finally, primary sludge (PS) was also treated at the previously selected conditions to evaluate the effects of this treatment on the PS characteristics and determine the general applicability of the developed sludge treatment technology on this sludge stream. (Chapter 6)

2.2.3 Cost analysis

Based on the experimental outcomes, the costs and the benefits generated by the newly developed technology were calculated. For the treatment by external acid dosing, the cost is from the consumption of the acid, alkali and nitrite, as well as the capital cost for installing the metal leaching reactor. For the treatment by ES, the costs are based on the consumption of electricity and
nitrite in the process as well as the capital cost for the configuration of the electrochemical reactor and the metal leaching reactor. For the calculation of the benefits, two scenarios were considered:

- **Sludge disposal without AD**

  Benefits are derived from: 1) sludge quality upgrade by toxic metal removal can reduce the cost of sludge disposal; 2) enhanced sludge dewaterability can reduce the (wet) amount of sludge requiring beneficial reuse or disposal and 3) the reduction in microbial contaminants can bring potential savings in the sludge stabilisation process required.

- **Sludge disposal after AD**

  The increased sludge digestibility can generate benefits from: 1) additional methane production to produce more energy (heat and electric power); 2) enhanced volatile solids destruction and possibly increased dewaterability of digested sludge can reduce the (wet) amount of final sludge for disposal; 3) the removal of toxic metals from sludge also can improve the sludge quality/grade to reduce the disposal costs.

The balance between the costs and the benefits was compared for evaluating the economic potential of the developed technology. (Chapter 7)
3. Enhancing toxic metal removal from acidified sludge with nitrite addition

Abstract

The production of sludge (biosolids) during wastewater treatment is a major issue for water utilities. A main issue limiting its beneficial reuse on agricultural lands is the presence of toxic metals. The currently used metal reduction technologies achieve insufficient removal of metals that are bound to the organic fraction of the sludge. In this chapter, a novel method that involves the addition of nitrite during sludge acidification to enhance metal removal was proposed and demonstrated. Using waste activated sludge collected from three full-scale wastewater treatment plants, it was found that acidification to pH 2.0 achieved good Zn solubilisation of around 70%, but only 3-7% of Cu was dissolved. Nitrite addition to the acidified sludge at a concentration of 20 mg NO₂⁻-N/L (equal to 19.2 mg HNO₂-N/L), substantially enhanced Cu removal to 45 - 64%, while Zn removal was also increased to over 81%. Metal distribution analysis using sequential chemical extraction revealed that the improvement of Cu and Zn removal was mainly due to the release of the organically bound metal fraction. It was hypothesised that free nitrous acid (HNO₂, FNA) may assist in the (partial) disruption of extracellular polymeric substances (EPS) and the subsequent release and solubilisation of fixed metals.

Redrafted and published in Environmental Science & Technology.

Fangzhou Du, Stefano Freguia, Zhiguo Yuan, Jürg Keller, Ilje Pikaar. Enhancing Toxic Metal Removal from Acidified Sludge with Nitrite Addition
3.1 Introduction

The presence of toxic metals in sludge often limits the opportunities for sludge reuse (Smith, 2009). The application of sludge to land is therefore stringently regulated in order to avoid long-term environmental problems. To remove metals from sludge, metal solubilisation, by either chemical leaching or bioleaching, followed by solid/liquid separation is the most commonly studied method, as reviewed in section 1.2.2. However, neither chemical leaching nor bioleaching has found widespread practical application, hindered by insufficient or slow removal or unstable performance, especially in removing metals associated with organics (Gheju et al., 2011).

Considering the limitations of both chemical leaching and bioleaching, there is a general interest in a more efficient method for toxic metal removal from sludge. In this chapter, a novel method to remove toxic metals from sludge through nitrite addition was proposed and demonstrated. At the low pH for metal leaching, nitrite could form free nitrous acid (FNA, HNO₂), which has been reported for its ability to disrupt extracellular polymeric substances (EPS) and microbial cells (Pijuan et al., 2012, Wang et al., 2013a, Wang et al., 2013b). Given that EPS are a significant sink for toxic metals in sludge (d'Abzac et al., 2013, Liu et al., 2001, Tian et al., 2006), it was hypothesised that by combining nitrite addition with acid leaching, the organically bound toxic metals in sludge could be released due to a disruption of the EPS matrix by FNA, thereby increasing the overall metal removal efficiency.

Therefore, the aim of this chapter was to determine the technical feasibility and economic potential of using nitrite for enhancing toxic metal removal from acidified sludge. The metal removal efficiency from sludge with and without nitrite addition during acidification was compared. To elucidate the effect of nitrite addition on the metal speciation in sludge, the toxic metal distribution in sludge was analysed by sequential chemical extraction. Finally, the metal removal efficiency at different nitrite concentrations and with exposure times was studied.

3.2 Materials and methods

3.2.1 Sludge source

Waste activated sludge (WAS) or thickened waste activated sludge (TWAS) was collected from three different full-scale wastewater treatment plants (WWTPs) in South-East Queensland, Australia. After collection, all sludge samples were immediately stored at 4 °C and used within 14
days of collection. All sludge samples were either concentrated (by settling) or diluted (using deionised water) to a total solids (TS) concentration of 20 - 30 g/L (2 - 3% dry solids), depending on the sludge sample used.

3.2.2 Toxic metal solubilisation from acidified sludge

Batch tests were conducted to assess the effect of nitrite addition on the toxic metal removal from acidified sludge. Sludge was acidified to pH 2 by dosing H₂SO₄ (9.2 M) and then NaNO₂ was added to achieve the nitrite concentrations of 20 mg NO₂⁻-N/L. Two control groups were set up: (i) raw sludge without chemical addition; (ii) sludge acidified to pH 2.0, but without nitrite addition. All tests lasted for 24 h, during which the sludge was continuously stirred. After treatment, sludge was immediately centrifuged at 13,000×g for 30 minutes (Centrifuge 5810R, Eppendorf, Germany), followed by the separation of supernatant and residue. The metals in the supernatant were considered as being solubilised and hence removed from the sludge. Experiments were set up and conducted in triplicate for all 3 different sludges.

3.2.3 Metal distribution analysis

After the above sludge treatment, a sequential chemical extraction (SCE) procedure described by Sims et al. (1991) was used in order to investigate the metal distribution change in the sludge. The extraction procedures and the differentiated fractions are described in Table 3-1. SCE was performed in triplicate for each sample from the different WWTPs.

Table 3-1. SCE procedures

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
<th>Extracted Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 mL sludge was separated into two tubes (6 mL and 44 mL) and centrifugation was conducted for both of them at 13,000×g for 30 min. For the 6 mL sample, the metals in supernatant stood for the <strong>soluble fraction</strong> and metals in the residues stood for the sum of all the other fractions, marked as F0. For the 44 mL sample, the supernatant was discarded and the residue went to the next step.</td>
<td>Soluble</td>
</tr>
</tbody>
</table>
The residue was resuspended (fill up to 44 mL) with 0.5 M KNO₃, and then was incubated in room temperature with continuous shake. After 16 h, 44 mL of sludge sample was separated into two tubes (6 mL and 38 mL) and centrifugation was conducted for both of them at 13,000 × g for 30 min. The supernatant was discarded. For the 6 mL sample, the metals in the residues were marked as F₁. The difference between F₀ and F₁ (F₀ – F₁) stood for the metals in exchangeable fraction. For the 38 mL sample, the supernatant was discarded and the residue went to the next step.

<table>
<thead>
<tr>
<th>Exchangeable</th>
</tr>
</thead>
<tbody>
<tr>
<td>The residue was resuspended (fill up to 38 mL) with 0.5 M NaOH, and then was incubated in room temperature with continuous shake. After 16 h, 38 mL of sludge sample was separated into two tubes (6 mL and 32 mL) and centrifugation was conducted for both of them at 13,000 × g for 30 min. The supernatant was discarded. For the 6 mL sample, the metals in the residues were marked as F₂. The difference between F₁ and F₂ (F₁ – F₂) stood for the metals in organically bound fraction. For the 32 mL sample, the supernatant was discarded and the residue went to the next step.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organically bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>The residue was resuspended (fill up to 32 mL) with 0.05 M Na₂EDTA, and then was incubated in room temperature with continuous shake. After 6 h, 6 mL of samples was collected centrifugation was conducted at 13,000 × g for 30 min. The supernatant was discarded. The metals in the residues were marked as F₃. The difference between F₂ and F₃ (F₂ – F₃) stood for the metals in inorganically bound fraction.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inorganic Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

---

25
The metals in the residues (F3) were in the (insoluble) residues fraction. By analysing the concentration of metals in the residues of each extracting steps and calculating metals in each fraction by subtraction, the possible carryover of extracting solutions in each step could be minimised.

### 3.2.4 Effect of exposure time on metal removal

To determine the effect of the exposure time, the metal removal efficiency after different treatment times was analysed. 80 mL of sludge was treated at pH 2.0 and with 20 mg NO$_2^-$-N/L. Sludge samples were collected at 0.5 h, 1 h, 2.5 h, 4.5 h, 8 h, 12 h and 24 h after the start of the treatment. The metal removal efficiency at all of the above time was analysed.

### 3.2.5 Effect of nitrite concentration on metal removal

To investigate the effect of different nitrite concentrations on toxic metal removal, 30 mL of sludge was acidified to pH 2.0 and exposed to the following nitrite concentrations: 0, 5, 10, 20, 40 and 60 mg NO$_2^-$-N/L. The exposure time was fixed at 24 hours.

### 3.2.6 Analysis and calculation

#### 3.2.6.1 Sludge characteristics

Total chemical oxygen demand (TCOD) and soluble chemical oxygen demand (SCOD) of sludge was tested by Spectroquant® COD cell tests (Merck, range 500-10000 mg/L). For SCOD, samples were filtered using a 0.22μm syringe filter (Milipore, USA) prior to analysis. The TS and VS concentrations of the WAS were determined using standard methods (A.P.H.A. et al., 1998):
1) Clean crucible in 550 °C oven until its weight ($m_0$, g) will not change;

2) 10 - 20 mL of sludge was added into the crucible, record the total weight ($m_1$, g);

3) Dry the sludge sample in the 105 °C oven for 24 hours until the constant weight ($m_2$, g);

4) Place the crucible with sludge sample in 550 °C furnace for at least 4 h until the constant weight ($m_3$, g).

The TS and VS were calculated using the following equations, with the assumption that sludge density is approximately 1 kg/L (Metcalf et al., 2003):

$$
\text{TS (g/L)} = \frac{m_2 - m_0}{m_1 - m_0} \times 1000 \quad (3-1)
$$

$$
\text{VS (g/L)} = \frac{m_2 - m_3}{m_1 - m_0} \times 1000 \quad (3-2)
$$

Each sample was measured in triplicate.

### 3.2.6.2 Metal concentration and removal calculation

Inductively coupled plasma optical emission spectrometry (ICP-OES, 7300DV, PerkinElmer, USA) was employed to analyse solubilised and total metal concentrations. The supernatants and residues separated from the above mentioned centrifugation were analysed separately. 3.6 mL of supernatant was mixed with 0.4 mL of 70% HNO$_3$ and digested at 160 °C for 20 min (rising to 160°C for 10 min and holding at 160°C for another 10 min) by microwave (MarsXpress, CEM, USA). The solution after digestion was used for ICP-OES analysis, determining the metal concentration in the supernatant. The residue from centrifuging 6 mL of sludge was digested using 10 mL of 70% HNO$_3$ at 200°C for 30 min (rising to 200°C for 15 min and holding at 200 °C for another 15 min). The solution after digestion of the residue was analysed for metal concentrations using ICP-OES.

Removal efficiency (RE) was calculated according to Equation 3-3:

$$
RE = \frac{c_{m,s.}}{c_{m,s.} + c_{m,r.}} \times 100\% \quad (3-3)
$$

where $c_{m,s.}$ and $c_{m,r.}$ stand for the concentration of a metal in supernatant and residue (normalised by the initial sludge volume), respectively. The $c_{m,s.}$ and $c_{m,r.}$ values were normalised according to Equations 3-4 and 3-5, respectively:
\[ c_{m.s.} = c_{test \ values \ of \ supernatant} \times \frac{V_{supernatant \ digestion \ solution}}{V_{initial \ sludge}} \]  

\[ c_{m.r.} = c_{test \ values \ for \ residue} \times \frac{V_{residue \ digestion \ solution}}{V_{initial \ sludge}} \]  

where \( c \) stands for concentration and \( V \) stands for volume.

In all experiments, pH was measured using a handheld pH meter (pH meter 11 series, Oakton, Australia).

3.3 Results

Table 3-2 shows that in all three sludges used in this chapter, the concentrations of Cr, Ni and Pb were below their Grade A threshold values. This means these metals require no further removal for sludge reuse. However, none of the three sludges meets the Grade A or Grade B standards due to the relatively high Cu or Zn concentrations (meeting Grade C standard only). Cd concentration also marked WWTP3 sludge as Grade C. The observation is in agreement with literature that reported Cu or Zn concentrations in biosolids in Australia (McLaughlin et al., 2007, Pritchard et al., 2010). Considering the above, we paid particular attention to Cu, Zn and Cd (only for WWTP3 sludge) in this chapter.

Table 3-2. Sludge contaminant concentration values and biosolids grading thresholds

<table>
<thead>
<tr>
<th>Sludge</th>
<th>TS(^a) (g/L)</th>
<th>TCOD(^a) (g/L)</th>
<th>Contaminant concentration values(^b) (mg/kg Dry Solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>WWTP1</td>
<td>25.7±0.2</td>
<td>29.2±0.3</td>
<td>BDL(^c)</td>
</tr>
<tr>
<td>WWTP2</td>
<td>21.9±0.4</td>
<td>33.4±0.7</td>
<td>BDL(^c)</td>
</tr>
<tr>
<td>WWTP3</td>
<td>27.0±0.3</td>
<td>34.1±3.8</td>
<td>8</td>
</tr>
<tr>
<td>NSW-EPA</td>
<td></td>
<td></td>
<td>Grade A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grade B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grade C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grade D</td>
</tr>
<tr>
<td>C.E.C. Directive limit values</td>
<td>20-40</td>
<td>-</td>
<td>1000-</td>
</tr>
<tr>
<td>USEPA ceiling concentrations</td>
<td>85</td>
<td>-</td>
<td>4300</td>
</tr>
</tbody>
</table>

Note: a. With standard deviation from triplicate measurements
b. The contaminant concentration value = the mean of contaminant concentration + 2 × standard deviation of contaminant concentration, according to NSW-EPA (NSW-EPA, 2000)

c. Below detection limit. The detection limit of ICP-OES for Cd is 0.001 mg/L, which equals to 1.3 mg/kg DS and 1.5 mg/kg DS for WWTP1 and WWTP2, respectively.

### 3.3.1 Effect of nitrite addition on metal removal and distribution

Table 3-3 shows the Cu, Zn and Cd removal efficiency after (i) acidification and (ii) acidification plus nitrite treatment. It can be seen that addition of only a small amount of nitrite (20 mg NO$_2^-$-N/L) resulted in a significant increase in Zn ($p < 0.05$) and Cu ($p < 0.05$) solubilisation for all three sludges. By acid only treatment (pH 2.0), less than 10% of Cu was solubilised. With 20 mg NO$_2^-$-N/L, the removal of Cu increased to 47.4 ± 2.4%, 64.1 ± 7.6% and 44.5 ± 0.2%, respectively, for the three sludges. It appeared that Zn was removed more efficiently than Cu by acidification. At pH 2.0, about 70% of Zn was solubilised. An extra 10% - 15% of total Zn was removed with the addition of nitrite. For the Cd in WWTP3 sludge, the treatment by acidification with and without nitrite did not show a significant difference in the removal efficiency, achieving 84.2 ± 5.3% and 78.9 ± 4.2%, respectively. Since only one group of Cd data (WWTP3) was available (due to other sludges having Cd concentrations below the limit of detection), the Cd removal was not discussed further in this thesis.
Table 3-3. Toxic metal solubilisation from sludge (with standard deviation from triplicate tests)

<table>
<thead>
<tr>
<th>Sludge source</th>
<th>Treatment</th>
<th>Cu</th>
<th></th>
<th>Zn</th>
<th></th>
<th>Cd</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Soluble (mg/L)</td>
<td>Insoluble (mg/L)</td>
<td>Removal (%)</td>
<td>Soluble (mg/L)</td>
<td>Insoluble (mg/L)</td>
<td>Removal (%)</td>
</tr>
<tr>
<td>WWTP1</td>
<td>None</td>
<td>BDL</td>
<td>8.62±0.07</td>
<td>0</td>
<td>BDL</td>
<td>12.47±0.53</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>pH2 only</td>
<td>0.52±0.02</td>
<td>8.65±0.17</td>
<td>5.7±0.2</td>
<td>11.27±0.14</td>
<td>4.75±0.20</td>
<td>70.8±0.9</td>
</tr>
<tr>
<td></td>
<td>pH2 + Nitrite</td>
<td>4.59±0.23</td>
<td>5.00±0.35</td>
<td>47.4±2.4</td>
<td>13.36±1.18</td>
<td>3.06±0.14</td>
<td>81.5±7.2</td>
</tr>
<tr>
<td>WWTP2</td>
<td>None</td>
<td>BDL</td>
<td>14.76±0.35</td>
<td>0</td>
<td>BDL</td>
<td>11.31±0.24</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>pH2 only</td>
<td>1.13±0.04</td>
<td>14.43±0.29</td>
<td>7.3±0.3</td>
<td>9.72±0.06</td>
<td>2.84±0.57</td>
<td>77.5±0.5</td>
</tr>
<tr>
<td></td>
<td>pH2 + Nitrite</td>
<td>10.34±1.23</td>
<td>5.79±0.58</td>
<td>64.1±7.6</td>
<td>10.51±0.14</td>
<td>1.72±0.09</td>
<td>86.0±1.1</td>
</tr>
<tr>
<td>WWTP3</td>
<td>None</td>
<td>BDL</td>
<td>8.58±0.62</td>
<td>0</td>
<td>BDL</td>
<td>16.16±1.30</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>pH2 only</td>
<td>0.27±0.04</td>
<td>9.08±0.46</td>
<td>2.9±0.4</td>
<td>12.23±0.08</td>
<td>5.81±0.31</td>
<td>67.8±0.4</td>
</tr>
<tr>
<td></td>
<td>pH2 + Nitrite</td>
<td>3.81±0.02</td>
<td>4.74±0.17</td>
<td>44.5±0.2</td>
<td>14.93±0.53</td>
<td>2.96±0.15</td>
<td>83.5±3.0</td>
</tr>
</tbody>
</table>

Note:  

a. Below detection limit. The detection limits of soluble fractions are 0.007 mg/L, 0.005 mg/L and 0.003 mg/L for Cu, Zn and Cd, respectively.

b. Final concentration of 20 mg NO₂⁻-N/L.

c. Below detection limit. The detection limit of insoluble fraction are 0.033 mg/L for Cd.
Figure 3-1 shows the Cu and Zn distribution after acidification with and without nitrite addition. In all three sludges, almost all the Cu was initially fixed in the solid phase, with the organically bound fraction clearly representing the dominant part (60.2 ± 3.0%, 68.1 ± 1.8% and 56.9 ± 4.9% of total Cu). The acidification-only treatment did not cause obvious changes to any fraction. Conversely, with the addition of nitrite, the organically bound fraction of Cu dropped to 43.7 ± 2.3%, 17.0 ± 3.5% and 37.7 ± 2.6%. The release of organically bound Cu was clearly contributing considerably to the improved solubilisation. In raw sludge, more Zn was present in the inorganically bound fraction, about 40% for all sludge samples. Around 16% - 30% of Zn was in the organically bound fraction. After treatment at pH 2.0 without nitrite, the removal of Zn reached about 70%. The inorganically bound fraction decreased to less than 5%. The fraction of organically bound Zn also decreased to 5% - 15%. The treatment with nitrite decreased the organically bound Zn to less than 5%.
Figure 3-1. The change of distribution of metals in sludges from all 3 WWTPs after 24 hours of treatment with acidification and acidification + nitrite addition. (A) for Cu and (B) for Zn. Raw: control group without any treatment. pH2: sludge was maintained at pH 2.0 for 24 h. pH2 + nitrite: sludge was maintained for 24 h at pH 2.0 with a nitrite concentration of 20 mg NO\textsubscript{2}^-/N/L. Error bars show standard deviation from triplicate tests.

3.3.2 Effect of nitrite exposure time and nitrite concentration

Figure 3-2 shows the effect of nitrite exposure time on metal removal. In all cases, the leaching process was relatively fast in the first 2.5 h. Even though the removal efficiency kept increasing until 24 h, the leaching process became slow after 2.5 h and did not progress much further after 4.5 h. Therefore, for practical applications a shorter treatment time of around 5 hours would be sufficient to achieve the desired metal solubilisation.
Figure 3-2. The Cu and Zn removal efficiencies varying with treatment duration (0.5 - 24 h). The sludge treatment was conducted at pH 2.0 with nitrite addition at 20 mg NO$_2^-$-N/L.

Figure 3-3 displays the metal removal efficiencies at different nitrite concentrations, ranging from 5.0 to 60.0 mg NO$_2^-$-N/L. A low nitrite concentration of only 5.0 mg NO$_2^-$-N/L already had a significant effect on Cu solubilisation (i.e. from less than 10% to around 40%), which further increased to about 45-65% at a concentration of 10.0 mg NO$_2^-$-N/L. Further increase of the nitrite concentration did not result in higher removal efficiencies. The removal of Zn showed similar responses to the increase of nitrite concentration. Hence, these results suggest that 10 mg NO$_2^-$-N/L would already be sufficient in practical applications.

Figure 3-3. Effect of NO$_2^-$-N concentrations on Cu and Zn removal efficiencies. The treatment was conducted at pH 2.0 for 24 hours.
3.4 Discussion

3.4.1 Improvement to metal removal by nitrite

Acidification is a common method for removing toxic metals from sludge in laboratory scale studies. Principally, the solubilisation of metals by acid is achieved through two mechanisms: (i) adsorbed metals in the solid phase are displaced by protons, and (ii) inorganic metal precipitates are solubilised at low pH (Veeken and Hamelers, 1999). These are confirmed in this study. In particular, the inorganically bound Cu and Zn were both solubilised. Indeed, high-levels of Zn removal were achieved from all three sludges with pH 2.0 treatment due to the relatively high fraction of inorganically bound Zn in all sludges.

However, Cu was mainly present in the organically bound form. Acidification alone clearly failed to solubilise this fraction of Cu. In fact, the pH 2 treatment hardly made any changes to the organically bound fraction. In comparison, the addition of only 20 mg NO$_2^-$-N/L significantly enhanced ($p < 0.05$) the solubilisation of the organically bound Cu and Zn.

According to Henderson-Hasselbalch equation:

$$pH = pK_a + \log_{10}\left(\frac{[NO_2^-]}{[HNO_2]}\right)$$

where $pK_a = 3.34$ for NO$_2^-$ at 25 °C (temperature used in this study), [HNO$_2$] is the molar concentration of the HNO$_2$ (FNA) and [NO$_2^-$] is the molar concentration of NO$_2^-$. At pH 2.0, approximately 96% of the added nitrite would be present in the form of FNA. Therefore, FNA rather than nitrite is likely the actual factor for the improved metal removal.

EPS has been considered as the sink for toxic metals in many studies (d’Abzac et al., 2013, Liu et al., 2001, Tian et al., 2006). The release of organically bound metals in the presence of FNA, which did not occur at the same pH without nitrite, suggests that FNA likely reacted with EPS leading to its breakdown. This is in agreement with a previous study, which showed that FNA treatment of sludge reduced the sizes of sludge flocs (Wang et al., 2013b). Further supporting evidence is that FNA assisted to solubilise the same fraction of metals that was solubilised by NaOH. In the fractionation process, 0.5 mol/L of NaOH was employed to extract organically bound fraction of metals. NaOH is known to have the ability to solubilise EPS (McSwain et al., 2005, Wei et al., 2012).
In addition, the mechanism of how nitrite or FNA treatment affects the sludge characteristics, especially the EPS fraction, is still unclear and will require further detailed studies.

Nitrite has the capacity of complexing transition metal ions, such as Cu$^{2+}$ and Zn$^{2+}$ with the stability constants ($\log_{10}$ value) of 1.34 and 0.37 respectively at 25 °C (Pettit and Powell, 1999). FNA (HNO$_2$) is a weak acid and could be considered as a complexing compound as well, with a stability constant of 3.34 ($\log_{10}$ value) at 25 °C. When nitrite is considered as a ligand, the higher stability constant value for H$^+$ indicates that the binding force of nitrite with H$^+$ is larger than its binding force with Cu and Zn. Under the experimental conditions applied in this study, i.e. H$^+$ concentration of 10 mM (pH 2) at a nitrite concentration of 0.7 - 1.4 mM, the capacity of nitrite ions to form complexes with Cu$^{2+}$ and Zn$^{2+}$ is expected to be negligible. The iron content of all three sludge was in the range of 6 - 20 mM, 1 - 2 orders of magnitude higher than the concentrations of Cu$^{2+}$ and Zn$^{2+}$. Considering this concentration and the stability constant of iron with nitrite of 2.59 ($\log_{10}$ value) (Pettit and Powell, 1999), it can be assumed that if any complexing of nitrite with metals would take place it would occur with iron rather than Cu and Zn.

### 3.4.2 Practical implications

This research lays the foundation for the development of a cost-effective technology for enhancing metal removal from wastewater sludge. Built upon the currently established technology for metal removal through acidification, this new technology involves adding a small amount of nitrite of around 10 g NO$_2^-$-N per m$^3$ of sludge at 2 - 3% dry solids during the acidification process. This amounts to a dose rate of about 0.4 g NO$_2^-$-N per kg of dry sludge. Sodium nitrite is currently available in the market at AUD450 per ton (or AUD2.20 per kg of NO$_2^-$-N) (Table 3-3). The cost for nitrite addition is negligible at AUD0.02 per m$^3$ of sludge (or AUD0.80 per ton dry solids) treated, which represents 1.4% of the costs associated with acidification and later neutralisation (Table 3-4). However, the quality of all three sludges was improved from Grade C to Grade B (Table 3-1), which was not achieved with acidification alone. The expense for nitrite dosing would be much lower than other metal removal strategies, such as H$_2$O$_2$, where the required final concentration of H$_2$O$_2$ is higher than 10 g/kg dry solids (Beauchesne et al., 2007, Dewil et al., 2007, Ito et al., 2008, Neyens et al., 2003).

<table>
<thead>
<tr>
<th>Table 3-4. Chemical cost for nitrite-based sludge treatment</th>
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<tbody>
<tr>
<td><strong>Items</strong></td>
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To avoid possible negative consequences from the sulfate addition into sludge, hydrochloric acid could be used for acidification, considering that hydrochloric and sulfuric acids have comparable metal leaching performances (Marchioretto, 2003) and both are commonly used inorganic acids. Assuming a sludge concentration of 2.6% (based on the TS concentration of sludge from WWTP1) during acidification + nitrite treatment, the chemical costs would be about AUD60 per tonne of dry sludge (Table 3-3). Considering that the final sludge cake for disposal has a TS concentration around 20%, the chemical cost will be about AUD12 per wet ton. The improvement of the sludge quality (i.e. from Grade C to Grade B) makes it possible to dispose it in locally available urban areas rather than more distant areas, leading to substantially reduced disposal costs, e.g. from AUD65 per wet ton to AUD50 per wet ton (Batstone et al., 2011). In addition, due to the lower metal concentration, more sludge could be applied on the land without exceeding the allowed cumulative metal pollutant loading rate. For locations where land availability is limited, this would as such represent an additional benefit. Overall, it can be concluded that the method proposed and demonstrated in this chapter is technically feasible and may provide an economically attractive alternative for metal removal from wastewater sludges compared to existing options. A long-term pilot-scale study will be needed to further investigate the economic potential of this technology for practical application.

<table>
<thead>
<tr>
<th>Sludge amount (DS)</th>
<th>1 t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge TS concentration</td>
<td>25.7 g/L</td>
</tr>
<tr>
<td>$H^+$ consumption to reach pH 2.0$^a$</td>
<td>2282 mole</td>
</tr>
<tr>
<td>Equivalent 32% HCl consumption</td>
<td>260 kg</td>
</tr>
<tr>
<td>NaNO$_2$ consumption at 10 mg NO$_2^-$-N/L</td>
<td>1.9 kg</td>
</tr>
<tr>
<td>90% lime consumption for neutralisation</td>
<td>71 kg</td>
</tr>
<tr>
<td>Price$^b$ of 32% HCl</td>
<td>200 AUD/tonne</td>
</tr>
<tr>
<td>Cost of HCl</td>
<td>52 AUD</td>
</tr>
<tr>
<td>Price$^b$ of NaNO$_2$</td>
<td>450 AUD/tonne</td>
</tr>
<tr>
<td>Cost of NaNO$_2$</td>
<td>0.86 AUD</td>
</tr>
<tr>
<td>Price$^b$ of Lime</td>
<td>100 AUD/tonne</td>
</tr>
<tr>
<td>Cost of Lime</td>
<td>7.1 AUD</td>
</tr>
<tr>
<td>Total cost (AUD)</td>
<td>60 AUD</td>
</tr>
</tbody>
</table>

Note:  

a. Based on the titration experiment of WWTP1 sludge  

b. From http://www.alibaba.com
Unlike many other studies using digested sludge (Babel and del Mundo Dacera, 2006, Pathak et al., 2009), it was proposed to use fresh secondary sludge (undigested) for the purpose of toxic metal removal. Compared to digested sludge, undigested sludge has a lower buffer capacity (Jenkins et al., 1981), leading to less acid consumption for pH adjustment and consequently lower costs. In addition, a negligible sulfide concentration is expected to be present in fresh secondary sludge since it is generated directly from aerobic processes. Therefore, the fraction of sulfide bound metals could be minimised, making solubilisation of metals more readily achievable. More importantly, the treatment of secondary sludge by nitrite could not only improve the toxic metal removal, but may potentially significantly reduce sludge production (Pijuan et al., 2012, Wang et al., 2013b), increase methane production during the following anaerobic digestion (Wang et al., 2013a), generating multiple benefits from the single treatment. The small amount of added nitrite could also be diluted and removed during anaerobic digestion (Wang et al., 2013a), eliminating the possible toxicity. These aspects will be investigated in the following chapters.

3.5 Conclusions

In this chapter, a method for enhancing the removal of toxic metals from activated sludge was proposed and experimentally demonstrated. The main conclusions are:

- Nitrite addition to acidified sludge (i.e., pH 2.0) substantially increases the solubilisation of organically bound copper and zinc, thus enhancing the overall removal of these toxic metals and improving the reuse opportunities of the sludge.

- Nitrite addition at 10 mg NO$_2^-$-N/L and a treatment time of 5 h are adequate for achieving the full potential of the method. Therefore, the new method incurs negligible additional costs in comparison to the currently established metal removal method through acidification.
4. *In situ* acidification and alkali production by an electrochemical system for toxic metal removal from sludge

Abstract

The consumption of corrosive acid and alkali for toxic metal removal from sludge, as well as the possible occupational health and safety issues when handling them, hinders the application of toxic metal removal treatments. To solve this problem, a three-compartment electrochemical system (ES) was employed for *in situ* acidification and alkali generation for metal solubilisation and removal from sludge. Acidification (to pH 2) of waste activated sludge (WAS) and alkali production were achieved in the anode and cathode compartment, respectively. Maintaining the optimised WAS treatment conditions determined in chapter 3 (5 h at pH 2 with 10 mg NO₂⁻-N/L) achieved a solubilisation of Cu and Zn of 60 ± 2% and 86 ± 1%, respectively, which was even higher than that achieved by external acid dosing. By centrifuge, the sludge liquor (aqueous phase of sludge) with solubilised metals was separated from sludge solids and was used as the catholyte of an electrochemical system. The pH of sludge liquor was raised up to pH 14 and the solubilised metals were precipitated and removed. The peak removal efficiency achieved for Cu and Zn were 74 ± 1% and 100%, respectively.
4.1 Introduction

In chapter 3, it was revealed that the treatment at pH 2 with the addition of small amounts of nitrite (i.e. 10 mg NO₂⁻-N/L) was able to significantly enhance toxic metal removal from waste activated sludge (WAS). Although the finding represents a major step forward for sludge management for water utilities, it still does not avoid the use of chemicals (i.e. acid and alkali). In addition to the costs of purchasing those chemicals, the needs for transport, storage and handling of concentrated acid and alkali come with serious occupational health and safety (OH&S) concerns.

To eliminate the expense and possible OH&S issues from using strong acids and alkali solutions, it is proposed in this chapter the in situ acidification of sludge and alkali production by an electrochemical system (ES) for sludge treatment. Pikaar et al. (2011b) employed a membrane separated ES and successfully achieved in situ alkali generation from sewage. Later, they observed the accumulation of protons in the anode compartment from the oxidation of sewage when accidental blockages occurred in the anode compartment, preventing flow (Pikaar et al., 2012). Similarly, acidification through anodic oxidation of waste activated sludge (WAS) is also theoretically possible and can be used for metal solubilisation. In addition, the possible production of reactive oxygen species (such as OH⁻ radicals) (Chen, 2004) and chlorine (Kraft, 2008) could also interact with the organics in the sludge and affect metal binding characteristics of sludge. The simultaneous alkali production in the cathode compartment could be used for metal removal and sludge neutralisation in the later stage of sludge management.

This chapter aims to investigate the feasibility of an integrated approach for sludge treatment by means of in situ electrochemical sludge acidification and metal removal by demonstrating the principles of operation. A three-chamber electrochemical system was set up with a anion exchange membrane (AEM) and a cation exchange membrane (CEM) separating the anode, middle and cathode compartments. WAS was acidified in the anode compartment by the anodic process and then treated with nitrite addition to solubilise metals. The performance of heavy metal solubilisation was studied and compared with acidification by hydrochloric acid dosing. Then the precipitation of solubilised metals in the cathode compartment was also investigated.
4.2 Materials and methods

4.2.1 Sludge source

Waste activated sludge was collected from a full-scale WWTP in South-East Queensland, Australia. After collection, all sludge samples were immediately stored at 4 °C and used within 14 days of collection. The main characteristics of the WAS were: total solid (TS) 21.3 ± 0.1 g/L; volatile solid (VS) 17.3 ± 0.1 g/L; total chemical oxygen demand (TCOD) 28.0 ± 0.1 g/L; soluble chemical oxygen demand (SCOD) 0.84 ± 0.10 g/L, pH 6.5 ± 0.3. The concentration of common heavy metals found in sludge is presented in Table 4-1. All the sludge characteristics were analysed in triplicate.

Table 4-1. Concentration of toxic metals in WAS

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration(^a) (mg/kg Dry Solids)</th>
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<tbody>
<tr>
<td>Cd</td>
<td>BDL(^b)</td>
</tr>
<tr>
<td>Cr</td>
<td>66 ± 3</td>
</tr>
<tr>
<td>Cu</td>
<td>518 ± 29</td>
</tr>
<tr>
<td>Pb</td>
<td>74 ± 1</td>
</tr>
<tr>
<td>Ni</td>
<td>35 ± 1</td>
</tr>
<tr>
<td>Se</td>
<td>BDL(^b)</td>
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<tr>
<td>Zn</td>
<td>768 ± 45</td>
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</table>

Note: a) With standard deviation from triplicate tests  
\(b\) Below detection limit.

4.2.2 Electrochemical system and operation

A three-compartment electrochemical cell was configured using Perspex frames with internal dimensions of 20 × 5 × 1.1 cm for all the three compartments (Figure 4-1). An anion exchange membrane (AEM, Ultrex AMI-7001, Membranes International Inc., USA) was used to separate the anode and middle compartments, whereas a cation exchange membrane (CEM, Ultrex CMI-7000, Membranes International Inc., USA) was used to separate the cathode and middle compartments. The effective surface area of the AEM and CEM exposed to liquid was 20 × 5 cm. A mesh shaped IrO\(_x\) coated titanium electrode (thickness: 1 mm; specific surface area: 1.0 cm\(^2\)/cm\(^2\), Magneto Anodes BV, The Netherlands) was used in the anode compartment. A stainless steel mesh electrode (6 mm mesh size, 0.8 mm wire) was used as the cathode. The projected surface area for both anode and cathode was 24 cm\(^2\) (4.8 cm × 5 cm). An Ag/AgCl reference electrode (RE-5B, Bio Analytical, USA) was placed in the anode compartment. Its potential was estimated at +197 mV versus a Standard Hydrogen Electrode (SHE). Both the anode and cathode compartments were fitted with a 500 mL buffer flask for recirculation. A 1 L buffer flask was used for the recirculation of the middle compartment. To avoid pressure build-up due to the production of oxygen (anode) and hydrogen
gas (cathode), water-locks were used in both the anode and cathode loops. A 5 M NaOH solution was used in the anode water-lock to absorb any chlorine gas formed. The oxygen and hydrogen formed were vented to the atmosphere.

**Figure 4-1.** Schematic diagram of the electrochemical system for metal removal from sludge

Figure 4-1 shows an overview of the experimental operation. 300 mL of WAS, 1 L of 60 g/L NaCl solution and 330 mL of sludge liquor (separated from sludge after anodic treatment, see the detailed procedures in the next paragraph) were in the anode, middle and cathode systems, respectively. The experiments were galvanostatically controlled at a fixed current of 240 mA (10 mA/cm²) using a Wenking potentiostat/galvanostat (KP07, Bank Elektronik, Germany). In all three compartments, the pH was monitored on-line (miniCHEM-pH, TPS, Australia). The anode potential, cathode potential and cell voltage were recorded every 30 seconds using a data acquisition system (34970A Data Acquisition Unit, Agilent Technologies, USA). During each experimental run, 5 mL of sample was collected from the cathode compartment every 10 minutes. Samples were immediately filtered through disposable Millipore filter units (0.22 μm pore size, Millipore Express, USA) and the filtrate was analysed for toxic metal concentration. During the process of electrochemical treatment,
the recirculation in all three compartments was achieved by a peristaltic pump (Masterflex pump, Extech Equipment Pty. LTD., Australia) at a flow rate of 220 mL/min.

The electrochemical cell was running until the WAS reached a pH of 2 in the anode compartment. The current was subsequently turned off, whereas the sludge was maintained at pH 2 for 5 hours either with or without nitrite addition of 10 mg NO\textsubscript{2}^- N/L. Then sludge was centrifuged at 13,000 \times g for 20 min (Centrifuge 5810R, Eppendorf, Germany) to be separated into sludge solids (with less metals) and acidic sludge liquor (with solubilised metals). Sludge liquor with metals then went to the cathode compartment for the electrochemical treatment mentioned in the above paragraph. After the electrochemical treatment in cathode compartment, sludge liquor became alkaline and was centrifuged at 13,000 \times g for 20 min (Centrifuge 5810R, Eppendorf, Germany), separating metal precipitate from sludge liquor. The sludge liquor was then mixed with the sludge solids to produce a sludge with neutral pH.

4.2.3 Sludge treatment

To investigate the effect of ES treatment on sludge metal removal, 4 different treatment conditions were investigated and compared with the untreated sludge (control):

A. HCl acidified sludge at pH 2 for 5 h
B. HCl acidified sludge at pH 2 with 10 mg NO\textsubscript{2}^- N/L for 5 h
C. ES acidified sludge at pH 2 for 5 h
D. ES acidified sludge at pH 2 with 10 mg NO\textsubscript{2}^- N/L for 5 h

In all experiments, HCl acidification was conducted by dosing 1 M hydrochloric acid. The nitrite concentration and the treatment duration were determined according to the results of chapter 3. All experiments were conducted in triplicate with 500 mL of WAS for each replicate.

4.2.4 Analytical methods and calculations

Sludge characteristics, including TS/VS and TCOD/SCOD, were measure according to section 3.2.6.1.

For the electrochemical cell, the major reaction on the anode and cathode were assumed to be:
Anode: \[ 2\text{H}_2\text{O} \rightarrow 4\text{e}^- + 4\text{H}^+ + \text{O}_2 \] (4-1)

Cathode: \[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \text{ (or 2H}^+ + 2\text{e}^- \rightarrow \text{H}_2) \] (4-2)

Based on the theoretical \( \text{H}^+ \) (or \( \text{OH}^- \)) production in the anode (or cathode) by the electrochemical reactions and the actual amount of \( \text{H}^+ \) (or \( \text{OH}^- \)) required for changing the pH of sludge in the anode (or sludge liquor in the cathode) as gained by titration, current efficiency (CE) was calculated via equation 4-3:

\[
CE_{\text{anode (or cathode)}} = \frac{V \cdot c \cdot F}{I \cdot t} \times 100\%
\]

where \( V \) stands for the volume of hydrochloric acid (or NaOH solution) consumed to titrate sludge (or sludge liquor) to the same final pH as in the electrochemical cell; \( c \) stands for the concentration of hydrochloric acid (or NaOH solution) used in the titration; \( F \) is the Faraday constant (96485 C/mol); \( I \) stands for the applied current (constant) and \( t \) stands for the reaction time. In this chapter, 1 M hydrochloric acid and 1 M NaOH were employed to titrate sludge at the anode and sludge liquor at the cathode, respectively.

Toxic metal concentration and removal efficiency were measured and calculated according to section 3.2.6.2.

4.3 Results and discussion

4.3.1 Sludge acidification and ES performance

In the anode compartment of the electrochemical cell, sludge was successfully acidified to the desired level, \( i.e. \) pH 2, within 140 min, as shown in Figure 4-2.

Figure 4-3 shows the electrode potentials and cell voltage during the operation of the ES. The anode potential was steady around +2.1 V (vs. SHE) in all six experimental runs, while the cathode potential, with and without nitrite addition, fluctuated between -2.0 and -3.5 V (vs. SHE).
Figure 4-2. pH of sludge in the anode compartment during ES operation

Figure 4-3. The electrode potential and cell voltage during the operation of ES. Error bars show the standard deviation.

Based on the assumption that the pH change in the anode and cathode was due to the acid/alkali production as described in equations 4-1 and 4-2, the CE was calculated based on the titration of the anolyte and catholyte, achieving $85 \pm 5\%$ and $85 \pm 10\%$ (n=6) for the anodic and cathodic process, respectively.
4.3.2 Metal solubilisation

Based on the comparison between the metal concentrations in sludge and the sludge grading thresholds (Table 1-1), the sludge used in this chapter was classified as grade C because of the Cu and Zn concentrations. All other metals were well below grade A threshold. Cu and Zn were also commonly reported as the problematic metals in other research work on biosolids in Australia (McLaughlin et al., 2007, Pritchard et al., 2010). Therefore, in this chapter, particular attention was paid to the solubilisation and removal of Cu and Zn.

The metal solubilisation efficiency is presented in Figure 4-4. Acidification by HCl rarely solubilised any Cu. But in the WAS acidified in the ES, 44 ± 12% of Cu was solubilised. When nitrite was added into the HCl acidified sludge, a significant increase ($p < 0.05$) of Cu solubilisation of 26 ± 3% was observed. Interestingly, the combination of ES acidification with nitrite delivered an even better Cu solubilisation, reaching 60 ± 2%. Zn was easier to solubilise. In HCl acidified sludge, the Zn solubilisation was 53 ± 2% and 65 ± 2% in the treatment without and with nitrite addition, respectively. Again, the ES acidification outperformed the HCl acidification, solubilising 74 ± 5% of the sludge Zn. The highest solubilisation for Zn was 86 ± 1%, achieved by ES acidification with nitrite addition.
The advantage of ES acidification on Cu and Zn solubilisation was clearly evident, compared with normal acid leaching by hydrochloric acid, either with or without nitrite. This indicates that some other process(es), beside that shown in Equation 4-1, must have also contributed to the metal solubilisation, especially considering the fact that the anode CE was 85 ± 5% for acid generation. At the anode potential of around +2.1 V (vs. SHE), many other reactions could be driven by the current, including chlorine generation from chlorides (Kraft, 2008). Chlorine and the likely formed hypochlorite are strong oxidative agents, which are able to oxidise organics in sludge (Saby et al., 2002, Wei et al., 2003). Organic compounds are important contributors of fixing metals in sludge (d’Abzac et al., 2013, Tian et al., 2006). Therefore, the oxidation of organics may have caused the additional release of organically-bound metals, leading to a better solubilisation. The addition of nitrite enhanced the metal solubilisation further. As discussed in chapter 3, the enhancement was hypothesised to be mainly the result of the formation of free nitrous acid (FNA) from nitrite at pH 2 and the consequential release of metals bound to the extracellular polymeric substance (EPS) present in the sludge.

Figure 4-4. Metal solubilisation for Cu (A) and Zn (B) after different treatments. Error bars show the standard deviation from triplicate solubilisation experiments.
4.3.3 Metal precipitation in the cathode compartment

OH\(^-\) was produced (or H\(^+\) was consumed) in the cathode compartment as described in Equation 4-2. Within 120 min, the pH of the sludge liquor increased from around 2 to 11-12, resulting in the precipitation of solubilised Cu and Zn ions (Figure 4-5). Zn was almost 100% precipitated and removed after the pH was restored to 7.2 and 7.8 for the sludge liquor without and with nitrite, respectively. The highest Cu removal, 74 ± 1% and 66 ± 4%, was obtained at pH 7.2 and pH 9.1 for the sludge liquor without and with nitrite, respectively. As the pH went higher, Cu was re-solubilised into the sludge liquor. Some studies reported that the optimum pH for Cu removal by hydroxide precipitation was around pH 7-11 (Chen et al., 2009, Fu and Wang, 2011). Lewis (2010) calculated the lowest copper hydroxide solubility was achieved at about pH 9 and a higher pH increased Cu solubility again. The final Cu removal efficiency after cathode treatment at pH 11-12 was between 59 ± 7% and 63 ± 4% for the catholyte without and with nitrite, respectively.

Figure 4-5. Metal concentration in aqueous phase (dots and solid lines) and pH change (dash lines) with time in cathode compartment
For the batch experiments in this study, the total reaction time for the electrochemical system was dependent on the anode process. Current was applied until the sludge in the anode reached pH 2. But the pH in the cathode already exceeded the optimum pH value (around pH 8) and reached higher than pH 12. Using sludge liquor (after separation of the solids) as the catholyte enabled metal precipitation in the cathode compartment and also on the cathode surface. White scale was observed on the cathode surface after the reaction, which could potentially passivate the electrode and reduce the electrochemical cell performance. Ter Heijne et al. (2010) reported the process of copper recovery by reducing Cu$^{2+}$ to Cu$^0$ on the cathode surface of a microbial fuel cell. A similar process of metal reduction might have also occurred in our study and contributed to the metal removal from the catholyte.

Lin et al. (2014) used clean water to produce up to about 3% of NaOH solution using a similar electrochemical system as described in this chapter, which provides an alternative option for the cathode process of ES sludge treatment. For practical applications, the in situ alkali production from clean water will make the cathodic process easier to handle compared to using the sludge liquor as the catholyte. Scaling on the cathode surface could be avoided and the pH could be controlled at the optimum level for metal precipitation in a separate process using the alkali solution generated in the cathodic compartment. Therefore, in the following studies, the ES was only used for sludge acidification and the metal precipitation and sludge neutralisation were conducted by NaOH solution. The cathodic process was not further investigated as part of this thesis.

4.4 Conclusions

A three compartment electrochemical system was configured for the in situ sludge acidification and alkali production to solubilise and remove toxic metals from waste activated sludge. The results led to the following key conclusions:

- Within 140 min, the anode process acidified sludge to pH 2, with an anodic current efficiency (for acid production) of 85 ± 5%.

- The metal solubilisation in the electrochemically acidified sludge was much better than in the HCl acidified sludge, achieving 60 ± 2% for Cu and 86 ± 1% for Zn when 10 mg NO$_2^{-}$-N/L was added.

- The cathodic process can generate alkali and remove the Cu and Zn solubilised in the anode process, ultimately reaching 74 ± 1% and 100% removal for Cu and Zn, respectively.
5. Acidification with nitrite addition significantly improves sludge digestibility, dewaterability and pathogen reduction

Abstract

The management of sludge is a major issue for water utilities. Sludge digestibility and dewaterability, as well as pathogen and toxic metal concentrations are the main factors determining the cost for sludge management. In this chapter, the effect of acidification with nitrite treatment, an effective method for toxic metal removal established in chapter 3 and 4, on sludge digestibility, dewaterability and pathogen removal were investigated. Waste activated sludge (WAS) from a full-scale waste water treatment plant was acidified by HCl dosing or in situ generated acid from an electrochemical system (ES) to pH 2 and treated with 10 mg NO₂⁻-N/L for 5 h. Then the digestibility of sludge after treatment was evaluated by biochemical methane potential (BMP) tests. The methane production from the WAS treated by ES acidification with nitrite and toxic metal removal was increased by 55% compared to untreated WAS. By fitting the experimental data to a first-order kinetic model, the biochemical methane potential of WAS was increased from 238 L CH₄/kg VS to 474 L CH₄/kg VS. The destruction of volatile solids (VS) in a 69 d BMP test increased from 42% to 65%. Furthermore, the solids content of belt filter dewatered sludge after treatment was increased from 14.6% to about 19%. At the same time, a 4-log reduction for the concentration of both total coliform and E. coli was achieved. This chapter shows the feasibility of acidification with nitrite addition to improve sludge digestibility, dewaterability and pathogen reduction simultaneously.
5.1 Introduction

In chapter 3, it was found that with a small amount of nitrite addition (10 mg NO$_2^-$-N/L), the removal of toxic metals was significantly enhanced. The enhancement was found to be related to the solubilisation of organically bound metals caused by the FNA formed at pH 2 with nitrite addition. In chapter 4, it was proven that the electrochemical system (ES) could be employed to acidify sludge in situ for metal solubilisation and precipitate solubilised metal ions for metal removal. The removal of toxic metals by ES acidification even showed advantage of further increasing metal removal compared to HCl acidification, most likely due to the direct/indirect oxidation of sludge organic matter during the anode process. As discussed in the section 3.4.2, the treatment conducted before anaerobic digestion (AD) may bring extra benefits for sludge management.

Mesophilic AD is a widely used approach for reduction and stabilisation of sludge. One of the main limitations of this process is the poor digestibility of waste activated sludge (WAS) (Appels et al., 2008). To improve the AD process, a variety of pre-treatment methods have been proposed including biological, thermal, mechanical and chemical processes, as reviewed in section 1.2.3.2. Recently, Wang et al. (2013a) reported that the treatment with free nitrous acid (FNA) significantly enhanced methane production from WAS at a FNA concentration of only 2 mg FNA-N/L (achieved by dosing 300 mg NO$_2^-$-N/L at pH 5.5) and the improvement increased with FNA concentration. In the chapter 3 and 4, the concentrations of FNA reached 9.6 mg FNA-N/L by adding only 10 mg NO$_2^-$-N/L at the pH 2. Whether the treatments employed in chapters 3 and 4 would also enhance the production of methane from the AD of WAS still needs to be verified. In addition, the in situ acidification of sludge by ES in chapter 4 was hypothesised to have an additional effect to sludge organic matters compared to acidification and nitrite addition. How the ES process could affect sludge digestibility is not clear yet.

Another critical factor for sludge management is sludge dewaterability, which has a significant effect on the sludge transport and disposal costs. After conventional dewatering, such as belt pressing and centrifugation, the water content of the sludge is still around 70 - 85 wt% (Wang et al., 2008). Hence, increasing the sludge dewaterability can reduce the mass of wet sludge produced (wet mass), thereby reducing transport and disposal costs. It has been previously reported that the sludge dewaterability can be affected by means of acid treatment (Chen et al., 2001, Zhou et al., 2014).
In addition, considering the strong biocidal effect of FNA (Jiang et al., 2011), a significant reduction in pathogen concentration in the sludge might also be achieved by the treatment at pH 2 with nitrite addition, which is required as a stabilisation process before land application (Sánchez-Monedero et al., 2004).

Therefore, the aim of this chapter is to investigate the effect of sludge acidification, both by HCl and ES in situ acidification, with nitrite addition on sludge digestibility, dewaterability and pathogen reduction. Waste activated sludge was treated by the optimised treatments as developed in chapters 3 and chapter 4. Then the digestibility and methane production from treated WAS through AD was evaluated using biochemical methane potential (BMP) tests. The effects of the treatment on sludge dewaterability and pathogen reduction were also studied.

5.2 Materials and methods

5.2.1 Sludge source

Waste activated sludge (WAS) was collected from a full-scale WWTP in South-East Queensland, Australia. After collection, all sludge samples were immediately stored at 4 °C and used within 14 days of collection. The main sludge characteristics were: total solids (TS) 21.3 ± 0.1 g/L; volatile solids (VS) 17.3 ± 0.1 g/L; total chemical oxygen demand (TCOD) 28.0 ± 0.1 g/L; soluble chemical oxygen demand (SCOD) 0.84 ± 0.10 g/L, and pH 6.5 ± 0.3.

All sludge characteristics were analysed in triplicate.

5.2.2 Sludge treatment

To investigate the effect of acidification and nitrite treatment on the sludge digestibility, dewaterability and pathogen reduction, the WAS was subjected to 6 different treatment and compared with the untreated WAS (control):

A. Untreated WAS (control);
B. HCl acidified WAS at pH 2 for 5 hours;
C. HCl acidified WAS at pH 2 with 10 mg NO$_2^-$-N/L for 5 h;
D. HCl acidified WAS at pH 2 with 10 mg NO$_2^-$-N/L for 5 h. Subsequently, the sludge was centrifuged at 13,000 xg for 20 min (Centrifuge 5810R, Eppendorf, Germany) to separate the WAS solids and the WAS liquor. The WAS liquor was neutralised to pH 7 to precipitate the metals. The precipitated metals were removed from the solution by filtration using Millipore filters (0.22 μm pore size, Millipore Express, USA). Subsequently, the filtrate and WAS solids were mixed (i.e. sludge with metals removed);

E. ES acidified sludge at pH 2 for 5 h;

F. ES acidified sludge at pH 2 with 10 mg NO$_2^-$-N/L for 5 h;

G. ES acidified sludge at pH 2 with 10 mg NO$_2^-$-N/L for 5 h. Subsequently, the same metal removal procedures as treatment D were performed and gain sludge with metals removed.

The nitrite concentration and treatment duration were selected according to the results in chapter 3 and 4. Acidification was achieved using 1 M HCl. The ES acidification was conducted as described in section 4.2. In all experiments, the neutralisation was performed by addition of 1M NaOH. All sludge treatment experiments were conducted in triplicate with 500 mL of WAS for each replicate. For all of those triplicates, the treated sludge was subsequently used in the following 3 series of experiments to determine their effects on the sludge digestibility, dewaterability and pathogen reduction.

5.2.3 Digestibility

The effect on the sludge digestibility was investigated using the biochemical methane potential (BMP) tests, as described by Jensen et al. (2011). The inoculum for BMP tests was collected from the mesophilic anaerobic digester at the same WWTP treating a mixture of WAS and primary sludge. The TS and VS content of the inoculum sludge were 24.6 ± 0.2 g/L and 16.8 ± 0.0 g/L, respectively.

For each BMP test, 50 mL of inoculum was used. Substrate (i.e. WAS from treatment A - G) was added at an inoculum to substrate ratio of 2.0 on a VS basis. The volume of each BMP vial was topped up with Milli-Q water to 80 mL. A blank was set up by mixing 50 mL of inoculum and 30 mL of Milli-Q water. The treated WAS (B - G) was neutralised to its initial pH 6.5 ± 0.3 before mixing with inoculum. To eliminate the possible effect on WAS caused by the shearing force during the centrifuge process in treatment D and G, WAS in all the other 5 treatment were also
centrifuged and mixed under identical condition (but without removing the metals) before BMP tests.

After filling with inoculum and substrate, the vials were flushed with nitrogen gas for 30 seconds at a flow rate of 3.5 L/min and then sealed with a butyl rubber stopper retained with an aluminium crimp-cap. An incubator maintaining 37 ± 1 °C was used to store all the testing vials. The BMP tests were terminated at 69 days when biogas production was negligible. The production of biogas (CH$_4$, H$_2$ and CO$_2$) was measured every 1 - 2 days over the first 10 days and every 4 - 6 days thereafter. The production of biogas was obtained by subtracting the average biogas production from gas production in the blank tests.

The BMP tests for each treatment were conducted in triplicate.

The apparent first order hydrolysis rate coefficient ($k$) and biochemical methane potential ($B_0$) were adopted as the key parameters for the assessment of WAS digestibility after different pretreatments. The values for these parameters were estimated by fitting BMP data to a first-order kinetic model using a modified version of Aquasim 2.1d with sum of squared errors ($J_{opt}$) as an objective function, as described by Batstone et al. (2009) and Jensen et al. (2011). The uncertainty surfaces of $B_0$ and $k$ was estimated based on a model-validity $F$-test with 95% confidence limits. An one-substrate model and a two-substrate model (Wang et al., 2013a) were used. The one-substrate model is described in Equation 5-1:

$$B(t) = B_0 \cdot (1 - e^{-k \cdot t})$$  \hspace{1cm} (5-1)

where $B(t)$ is the cumulative methane yield at time $t$ (L CH$_4$ / kg VS added); $B_0$ is the biochemical methane potential (the final methane yield); $k$ is the hydrolysis rate coefficient (d$^{-1}$); and $t$ is time (d). In the two-substrate model, two types of substrates, i.e. a rapidly degradable substrate and a slowly degradable substrate, were considered to exist in the WAS sample (Equation 5-2):

$$B(t) = B_{0,\text{rapid}} \cdot (1 - e^{-k_{\text{rapid}} \cdot t}) + B_{0,\text{slow}} \cdot (1 - e^{-k_{\text{slow}} \cdot t})$$ \hspace{1cm} (5-2)

where $B(t)$ is the cumulative methane yield at time $t$; $B_{0,\text{rapid}}$ is the biochemical methane potential of the rapidly degradable substrate; $k_{\text{rapid}}$ is the hydrolysis rate coefficient of rapidly degradable substrate; $B_{0,\text{slow}}$ is the biochemical methane potential of the slowly degradable substrate; $k_{\text{slow}}$ is the hydrolysis rate coefficient of the slowly degradable substrate; $t$ is time. Total biochemical methane potential is the sum of the rapidly and slowly degradable pools, i.e. $B_0 = B_{0,\text{rapid}} + B_{0,\text{slow}}$. 

52
5.2.4 Dewaterability

The belt filter proxy test described by Higgins et al. (2014) was adopted for sludge dewatering after the treatments A, B, C, E and F. The dewatering procedures are described below:

1) 50 mL of sludge was drained through a belt filter fabric. The solids on the fabric were moved around with a spatula to help with draining.

2) The wet solids cake was scraped onto the belt filter fabric in a centrifuge cup using a spatula and the solids were spread out over the whole fabric.

3) The centrifuge cups with wet solids cake and belt filter fabric were centrifuged sequentially: at 200 ×g for 2 min; at 500 ×g for 2 min and at 3000 ×g for 10 min.

The sludge cakes on the filter after the above procedures were considered as dewatered sludge. The dewaterability of sludge was determined by measuring the cake solids concentration (% w/w).

5.2.5 Pathogen concentration

Total coliform and E.coli were selected as two indicators of pathogens in WAS (NSW-EPA, 2000, USEPA, 1992). The effects of the different sludge treatments (A - C and E - F) on pathogen concentrations were analysed using the Colilert-18 kit test (IDEXX, U.S.A), according to Eccles et al. (2004). The WAS in treatment B, C, E and F was neutralised to its initial pH 6.5 ± 0.3 before tests.

5.2.6 Analysis and calculation

Sludge characteristics, including TS and TCOD, were measured according to section 3.2.6.

During the course of the BMP experiments, the gas phase pressure was measured by a manometer before each sampling event. The cumulative volume of the gas produced was calculated according to the pressure in the headspace (80 mL) and expressed under standard conditions (25 °C, 1 atm). The composition of the biogas produced (CH₄, CO₂, H₂) was analysed using a gas chromatograph with a thermal conductivity detector (GC-2014, Shimadzu, Australia), as described by Astals et al. (2015).
Through AD, the mass of sludge is reduced due to the degradation of VS into methane. The VS destruction can be calculated in accordance with Equation 5-3:

\[
VS\,\text{destruction}\,(\%) = \frac{B(t)}{380 \times 1.56} \times 100\%
\] (5-3)

where \(B(t)\) is the biochemical methane production at time \(t\) (L CH\(_4\)/kg VS added); 380 is theoretical biochemical methane potential under standard conditions (25 °C, 1 atm) (L CH\(_4\)/kg TCOD); 1.56 is the TCOD/VS ratio of the WAS used in this study.

5.3 Results and discussion

5.3.1 Enhancement on sludge digestibility

The cumulative methane production is shown in Figure 5-1. Throughout 69 d of BMP tests, the HCl acidification treatment (B) raised the production of methane by 5.9 ± 4.2%. With the same final pH and treatment duration, the ES acidification treatment (E) made the production of methane increased by 36.3 ± 3.2%, showing great advantage than HCl acidification. The addition of nitrite to the HCl acidified WAS (C) promoted additional growth to the methane production, achieving 28.0 ± 0.2% of increase compared to control. From the WAS after the treatment E (no nitrite) and F (with nitrite), the production of methane reached similar levels, around 337 - 344 L/kg VS added, indicating that nitrite addition did not lead to significant change \((p = 0.79)\). The greatest enhancement for methane production was observed in the treatment D and G where toxic metals were removed from sludge after acidification with nitrite treatment, reaching 45.7 ± 2.6% and 55.2 ± 6.0% of increase, respectively. The results obtained here clearly show the effect of nitrite addition and metal removal on the production of methane.
The hydrolysis rate coefficient \((k)\) and biochemical methane potential \((B_0)\) were estimated using both first-order one-substrate model and two-substrate model. The one-substrate model gave satisfactory fit to the experimental data of A and B treatment. Using an \(F\)-test hypothesising that two-substrate model was better than one-substrate model, there was insufficient evidence to support a two-substrate model for A and B \((p > 0.05)\). However, the treatments C ~ G had strong evidence of a two-substrate model \((p < 0.05)\) which delivered satisfactory fit (see Figure 5-1). The \(k\) of treatments A and B and the \(k_{\text{rapid}}\) of treatments C ~ G from the modelling estimation are presented in Table 5-1. All the treatments B ~ G increased the hydrolysis rate from \(0.26 \pm 0.02\ \text{d}^{-1}\) to a comparable level around \(0.36 - 0.41\ \text{d}^{-1}\).

The change of SCOD of sludge after treatments by different methods and the VS destruction calculated from the methane production are presented in Table 5-1.
Table 5-1. Sludge solubilisation after different treatment, VS destruction and estimated hydrolysis rate coefficient for BMP tests

<table>
<thead>
<tr>
<th>Sludge treatment</th>
<th>SCOD (mg/L)a</th>
<th>VS destructiona</th>
<th>Hydrolysis rate coefficient (k or $k_{\text{rapid}}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Control</td>
<td>842 ± 100</td>
<td>42 ± 1%</td>
<td>0.26 ± 0.02$^b$</td>
</tr>
<tr>
<td>B: HCl acidification</td>
<td>1950 ± 33</td>
<td>44 ± 2%</td>
<td>0.37 ± 0.04$^b$</td>
</tr>
<tr>
<td>C: HCl acidification + nitrite$^d$</td>
<td>1749 ± 17</td>
<td>53 ± 0%</td>
<td>0.41 ± 0.15$^c$</td>
</tr>
<tr>
<td>D: HCl acidification + nitrite +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>metal removal$^d$</td>
<td>1749 ± 17</td>
<td>61 ± 1%</td>
<td>0.38 ± 0.13$^c$</td>
</tr>
<tr>
<td>E: ES acidification$^d$</td>
<td>1793 ± 39</td>
<td>57 ± 1%</td>
<td>0.37 ± 0.11$^b$</td>
</tr>
<tr>
<td>F: ES acidification + nitrite$^d$</td>
<td>1971 ± 119</td>
<td>58 ± 5%</td>
<td>0.39 ± 0.15$^c$</td>
</tr>
<tr>
<td>G: ES acidification + nitrite +</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>metal removal$^d$</td>
<td>1971 ± 119</td>
<td>65 ± 2%</td>
<td>0.36 ± 0.15$^c$</td>
</tr>
</tbody>
</table>

Note:  
- a. Data were presented with standard deviation from triplicate tests  
- b. Estimated from one-substrate model with 95% confidence intervals based on a two-tailed t-test in parameter standard errors.  
- c. Estimated from two-substrate model and the value shows the $k$ of rapidly degradable substrates with 95% confidence intervals based on a two-tailed t-test in parameter standard errors.  
- d. The difference between the treatment and control was significant ($p < 0.01$)

After the treatment, the SCOD of WAS was increased from 842 mg/L to about 1750 - 1950 mg/L, indicating that the solubilisation of organics in all tests achieved to a similar level. Therefore, the increase of the hydrolysis rate of all the treatments were also reached a comparable level, which fitted the fact that the profiles of methane production after all the treatments, both experimental and estimated data, overlapped and all surpassed the methane production of control in the first few days of BMP tests.

The final increase of the methane production in the BMP tests indicated the increase of $B_0$ (total), resulting from that part of the refractory substrate of the sludge was converted to degradable substrate. The values of $B_0$ for all the treatments were compared in Figure 5-2, where error in two substrate models was based on the error in methane yields for rapid and slow substrates, with hydrolysis coefficients fixed to their optima. This was performed due to the high level of non-linearity in the parameter space. The $B_{0,\text{rapid}}$ of the treatments reached comparable values as the $B_0$
of the control. The increase of the final methane production mainly came from the addition of the slowly degradable substrates.

![Figure 5-2](image)

**Figure 5-2.** Estimated biochemical methane potential ($B_0$) of WAS from different treatment. Error bars show 95% confidence intervals.

The HCl acidification treatment only made the production of methane increased by 5.9%. The enhancement for methane production brought by the ES acidification treatment clearly outperformed the HCl acidification, similar trend of which had been observed in chapter 4 in the aspect of removal of toxic metals. During the anode process of the ES, the potentially generated strong oxidizing agents, such as free chlorine and OH· radical, are able to disrupt EPS in WAS. EPS is naturally refractory for anaerobic digestion (Carrère et al., 2010). The disrupted EPS was converted from non-digestible substrate to slowly degradable substrate and resulted in the improved sludge digestibility.

The addition of nitrite also resulted in a substantial increase for the production of methane, especially for HCl acidification treatment. As discussed in chapter 3, nitrite addition to acidified sludge released organically bound metals in sludge, which was believed due to the possible disruption of EPS caused by FNA originated from nitrite in the acidic condition. Again, the disruption of EPS improved the digestibility of WAS. FNA has been reported for its ability of
increasing biodegradability of sludge in both aerobic (Pijuan et al., 2012) and anaerobic (Wang et al., 2013a) conditions. In those studies, up to 900 mg NO$_2^-$-N/L of nitrite addition was required to reach the final FNA concentrations of about 2 mg FNA-N/L. Wang et al. (2013a) reported that sludge treatment at 50 - 300 mg NO$_2^-$-N/L at pH 5.5 resulted in higher SCOD concentrations compared to treatment at pH 5.5 without nitrite. Higher SCOD concentrations subsequently resulted in higher $k$ and $B_0$ values during the BMP test. In this chapter, the treatment at pH 2 with nitrite addition did not cause additional increase of SCOD of treated WAS or $k$ ($k_{rapid}$), compared to pH 2 only treatment. Conversely, the increase in total methane production and $B_0$ revealed that nitrite addition at pH 2 did result in enhancement to the digestibility of the insoluble fraction, converting part of non-degradable substrates into slowly degradable substrates. Hence, the results obtained in this study indicate that the effectiveness of nitrite at pH 2 is based on a different working mechanism than at pH 5.5. Further research is needed to reveal the nature of the effect of nitrite to sludge at pH 2.

Toxic metals, *i.e.* Cu, Zn, *etc.*, are known for their inhibitive effect to AD process, even when their concentration is lower than 10 mg/L (Wong and Cheung, 1995). The treatment at pH 2 with nitrite solubilised toxic metals in sludge. By the subsequent solid/liquid separation and precipitation, toxic metals were removed from sludge. As a result, the inhibition to AD by toxic metals was partially released, which was reflected by the increase of cumulative methane production for treatment D vs. C and G vs. F ($p < 0.05$).

### 5.3.2 Enhancement on sludge dewaterability

Figure 5-3 shows the solids content of sludge from different treatments after dewatering process. It can be seen that all the treatments at pH 2, both by HCl and ES acidification, achieved a similar final solids content of about 19%, presenting a significant ($p < 0.05$) increase compared to 14.6% of the untreated sludge. However, the addition of nitrite did not make any additional change for the solids content, indicating that the increase of dewaterability was mainly caused by the acidic condition. As a result of the improved sludge dewaterability, the production of wet sludge could be reduced by about 20%. Similarly, Chen et al. (2001) found that the treatment at pH 2.5 increased the solids content of sludge after dewatering from about 18% to 24%. However, they also observed that when the pH decreased further below pH 2.5 the sludge dewaterability decreased a bit. The identification of the optimum condition for sludge dewaterability enhancement requires further study.
Figure 5-3. Solids content of belt filter dewatered sludge from different treatment

5.3.3 Effects on sludge pathogen concentration

Before land application, the pathogen content in sludge is required to be reduced to a certain level to avoid the possible release of bio-hazards to environment, known as sludge stabilisation. Conventional sludge stabilisation includes lime treatment, aerobic/anaerobic digestion, thermal treatment and so on. In this chapter, the acidification with nitrite addition treatments reduced the pathogen concentrations, expressed as most probable number (MPN) per gram dry solids (DS) for total coliforms and E.coli in Figure 5-4. The acidification treatments by HCl and the ES had similar performance, resulting in the concentrations of total coliforms and E.coli reduced by 3 and 2 log units, respectively. With the addition of nitrite to the acidified sludge, the concentration abatement for these two pathogen indicators achieved additional 1 or 2 log units.

FNA has strong biocidal effect and was used to kill sewer biofilms at concentrations lower than 3 mg FNA-N/L (Jiang et al., 2011). At pH 2 with 10 mg NO$_2^-$-N/L addition (the condition in this chapter), the concentration of FNA was about 9.6 mg FNA-N/L (according to equation 3-6 in chapter 3), making substantial contribution for pathogen reduction. For the ES acidification, side reactions during anodic process also have disinfection effect, an important one of which could possibly be chlorine formation (Kraft, 2008). Chlorine is known as disinfection agent (Drogui et al., 2013) and could contribute to the pathogen reduction observed in this study. In addition, the
possible generation of reactive oxygen species (Chen, 2004) could also play a role in the elimination of pathogens. However, the similarity of the HCl and ES acidification indicated that the side reactions did not play a dominant role on pathogen reduction in this study.

Figure 5-4. Concentration of total coliforms and *E.coli* in sludge after different treatment

In this chapter, the pathogen reduction performance of the acidification with nitrite treatment was comparable to mesophilic aerobic/anaerobic digestion and heat (108 °C for 10 h) treatment achieving 2 - 4 log units of reduction (Gantzer *et al.*, 2001). But the treatment only last for 5 h, much shorter than conventional mesophilic AD (commonly around 20 days) (Appels *et al.*, 2008). However, the concentrations of the indicators were still higher than the threshold for Grade A standard according to NSW-EPA regulations (Faecal coliforms < 1000 MPN/g DS and *E.coli* < 100 MPN/g DS) (NSW-EPA, 2000). Therefore, further studies for optimizing the chemical dosage and treatment duration to achieve better pathogen reduction are warranted.
5.4 Conclusions

In this chapter, the effects of HCl and ES acidification with 10 mg NO$_2^-$-N/L nitrite on sludge digestibility, dewaterability and pathogen concentration were investigated. The main conclusions are:

- The treatment with ES acidification with nitrite and metal removal led to the highest methane production, achieving $384 \pm 8$ L CH$_4$/kg VS added after 69 d of batch BMP tests, which represented an increase of 55%. The VS destruction reached 65% after 69 d of AD.

- The TS content of the dewatered sludge after all the different treatments in this chapter increased to about 19%, compared to 14.6 ±1.4% for untreated sludge.

- The acidification with nitrite treatments strongly reduced MPN concentrations of pathogen indicators, *i.e.* total coliforms and *E.coli*, by 4 log units.
6. Electrochemical treatment to improve characteristics of primary sludge

Abstract

Acidification by HCl addition or the electrochemical system (ES) combined with nitrite addition was proven to be able to enhance toxic metal removal, pathogen reduction, digestibility and dewaterability for waste activated sludge in the previous chapters. In this chapter, the established treatment technology by acidification with nitrite was applied to primary sludge (PS) to verify its ability to improve the characteristics of PS for beneficial reuse. It was found that HCl acidification, either with or without nitrite addition, failed to remove Cu from PS, whereas the ES acidification with nitrite achieved a significant metal removal, 39 ± 1% and 82 ± 0.5% for Cu and Zn, respectively. Only minor effects on the PS digestibility and dewaterability were made by the treatment.
6.1 Introduction

In municipal wastewater treatment plants (WWTPs), about 50 - 70% of suspended solids are captured during the primary sedimentation, forming primary sludge (PS) (Metcalf et al., 2003). Even though it has been reported that toxic metal removal from wastewater is more efficient in secondary treatment with activated sludge process than the primary process (Brown et al., 1973), the concentrations of toxic metals in primary sludge are still considerable and no less than secondary sludge (Álvarez et al., 2002), which contributes largely to the concern about land application of wastewater sludge. PS is readily degradable and the solids amount could be reduced remarkably by anaerobic digestion (AD) due to the conversion of organic matter to biogas (Carrère et al., 2010). Conversely, toxic metals are non-degradable so the metals in PS may introduce even greater issues for sludge management after AD. However, research on the removal of toxic metals from PS has been rather limited.

In the previous chapters, it was found that the acidification by HCl and the electrochemical system (ES) with nitrite addition was able to remove the toxic metals from waste activated sludge (WAS) while enhancing pathogen reduction, dewaterability and digestibility simultaneously. However, the composition of WAS and PS are quite different (Gavala et al., 2003). Whether this novel technology is applicable to PS and how it will perform on improving the characteristics of PS still needs to be verified.

Therefore, the aim of this chapter is to investigate the performance of electrochemical acidification with nitrite addition on improving PS characteristics. The PS from a local WWTP was treated by acidification, both via HCl and the ES, with nitrite addition at the same conditions as in chapter 5. The metal removal efficiency was analysed. The proxy Belt filter dewatering was conducted on the treated PS and the solids content after dewatering was measured as the parameter for sludge dewaterability. At last, the treated PS was used as substrate for biochemical methane potential (BMP) tests to investigate the effect of the treatments on the sludge digestibility.

6.2 Materials and methods

6.2.1 Sludge source

Primary sludge (PS) was collected from a full-scale WWTP in South-East Queensland, Australia. After collection, sludge was stored at 4 °C before use and all the experiments started within 1 week.
from collection. The main characteristics of the PS were: total solid (TS) 29.9 ± 0.3 g/L; volatile solid (VS) 25.1 ± 0.2 g/L. The concentrations of common toxic metals are presented in Table 6-1. All the analysis was conducted in triplicate.

Table 6-1. Concentrations of toxic metals in PS

<table>
<thead>
<tr>
<th>Contaminant concentrations (mg/kg Dry Solids)a</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 ± 0.1</td>
<td>47 ± 2</td>
<td>421 ± 18</td>
<td>70 ± 5</td>
<td>27 ± 1</td>
<td>873 ± 45</td>
<td></td>
</tr>
</tbody>
</table>

Note: a. Presented as average with standard deviation from 12 tests

6.2.2 Sludge treatment

An electrochemical system (ES) for PS treatment was setup as described in section 4.2. To investigate the effect of different treatments on the metal removal, sludge dewaterability and digestibility, the PS was subjected to 5 different treatments and compared with the untreated PS (control):

A. No treatment, raw sludge (control group)
B. HCl acidified sludge at pH 2 for 5 h
C. HCl acidified sludge at pH 2 with 10 mg NO$_2^-$-N/L for 5 h
D. ES acidified sludge at pH 2 for 5 h
E. ES acidified sludge at pH 2 with 10 mg NO$_2^-$-N/L for 5 h
F. ES acidified sludge at pH 2 with 10 mg NO$_2^-$-N/L for 5 h. Subsequently, the sludge was centrifuged at 13,000 ×g for 20 min (Centrifuge 5810R, Eppendorf, Germany) to separate the PS solids and the PS liquor. The PS liquor was neutralised to pH 7 to precipitate the metals. The precipitated metals were removed from the solution by filtration using Millipore filters (0.22 μm pore size, Millipore Express, USA). After that, the filtrate and PS solids were mixed (i.e. sludge with metals removed).

The nitrite concentration and treatment duration was selected according to the results in chapter 3. HCl acidification was conducted by dosing 1 M hydrochloric acid. Neutralisation was performed by adding 1M NaOH solution. All the sludge treatments were conducted in triplicate with 500 mL of
PS for each replicate. The treated sludges were subsequently used in the following tests to determine the effects of the treatments on the toxic metal removal, sludge dewaterability and digestibility.

6.2.3 Analysis of the PS characteristics

6.2.3.1 Toxic metal removal

Toxic metal concentrations and removal efficiency were measured and calculated according to section 3.2.

6.2.3.2 Dewaterability

Sludges from treatments A - E were selected to investigate the effect of treatment on dewaterability. The Belt filter proxy test described in section 5.2.4 was used for sludge dewatering. The solids content (% w/w) of the dewatered sludge was measured as the parameter for dewaterability comparison.

6.2.3.3 Digestibility

To evaluate the effect of different treatments on sludge digestibility, the biochemical methane potential (BMP) test was adopted, as described in section 5.2.3. From the same WWTP where PS was collected, sludge effluent from the mesophilic anaerobic digester treating a mixture of PS and WAS was collected as the inoculum of BMP tests. The TS and VS concentrations of inoculum were 20.7 ± 0.5 g/L and 15.3 ± 0.4 g/L, respectively.

PSs after treatments A - F were used as substrates. Before the BMP tests, PSs after treatments B - F were neutralised to their initial pH 6.0 ± 0.3. PSs from treatments A - E were also centrifuged and mixed at the identical condition as F (but without metal removal) to eliminate the possible effect of centrifugation on digestibility.

80 mL of inoculum was added to each BMP test vial. Then the substrates were added into test vials with a volume determined according to an inoculum to substrate ratio of 2.0 on a VS basis. Milli-Q water was used to fill the final testing volume to 100 mL for each vial. A blank test was set up by using 20 mL of Milli-Q water as substrate. All tests were conducted in triplicate. The estimation of
the apparent first order hydrolysis rate coefficient \( (k) \) and biochemical methane potential \( (B_0) \) was conducted according to section 5.2.3.

### 6.2.4 Analytical methods and calculations

Sludge characteristics, including TS and TCOD, were measured according to section 3.2.

The production of biogas and composition was analysed according to section 5.2.

### 6.3 Results and discussion

#### 6.3.1 Metal removal

According to the initial metal concentrations in Table 6-1, only Cu and Zn exceeded the threshold for Grade B sludge. The concentrations of all the other metals were well below Grade A threshold, which would enable reuse for land application (Table 1-1). Therefore, this chapter will only focus on Cu and Zn removal.

Figure 6-1 presents the solubilisation efficiency of Cu and Zn after different treatments. It can be noticed that HCl acidification only solubilised about 32\% of Zn and almost no Cu. The addition of nitrite did not lead to any improvement to the metal solubilisation. This performance was quite different from previous study conducted with waste activated sludge (WAS) in chapter 3 and chapter 5, where more than 60\% of Zn could be solubilised by acid dosing and the addition of nitrite resulted in significant enhancement of the solubilisation of both Cu and Zn. However, the in situ acidification by the ES did solubilise Cu and Zn, achieving 28 ± 6\% and 79 ± 0.4\%, respectively. The highest solubilisation was observed in the treatment E (ES acidification with nitrite addition), removing 39 ± 1\% of Cu and 82 ± 0.5\% of Zn. Due to the successful Cu and Zn removal after the treatment E, the PS was upgraded from C to B according to the sludge grading threshold presented in Table 1-1.
Figure 6-1. Removal efficiency of Cu (A) and Zn (B) after different treatment
PS is mainly composed of suspended solids and organics already present in the raw wastewater. It was reported that the majority of Cu and Zn (about 80% and 50% respectively) in PS were present in the oxidisable fraction (Álvarez et al., 2002). The poor acid extractability of metals in oxidisable fraction led to the poor performance of acid metal leaching in this chapter, especially for Cu. This agreed with the results obtained for metal solubilisation from WAS by only acid leaching in chapter 3. However, the addition of nitrite did not enhance Cu and Zn solubilisation from PS, which was different from what was observed in chapter 3 where the solubilisation of Cu and Zn from WAS was significantly enhanced by nitrite addition. WAS basically contains living and dead biomass (Metcalf et al., 2003) and the extracellular polymeric substance (EPS) was believed to be the main sink for metals (d’Abzac et al., 2013, Tian et al., 2006). The free nitrous acid (FNA) formed from nitrite in acidic condition was likely to have caused the disruption of EPS and released the combined metals, which led to the improvement of metal removal for WAS. Since the EPS content in PS is not as rich as in WAS, the metal binding behaviour is different, leading to a different response to the nitrite addition for metal solubilisation.

When acidification was achieved by anodic process in the ES, not only H⁺ was produced but there was also possible generation of strong oxidative agents, such as chlorine and reactive oxygen species (Chen, 2004, Pikaar et al., 2011a). Given that the oxidisable fraction accounts for a large fraction of metal distribution in PS (Álvarez et al., 2002), the anodic process seemed to have turned the metals from unleachable fraction to leachable fraction. Subsequently, the metals were solubilised during the treatments at pH 2 treatment.

6.3.2 Sludge dewaterability

The solids content of wet sludge from different treatments after dewatering process is presented in Figure 6-2. The solids content of the initial sludge achieved 29.8 ± 0.7%. All the treatments underwent a significant increase (p < 0.05) in the solids content to a comparable level of 32.5 ± 1.0%, indicating the corresponding improvement of sludge dewaterability. Thereby, the production of wet PS could be reduced by 9.1% by the treatments used in this study. Considering that all the treatment achieved a similar increase for sludge dewaterability, it is believed that the pH change had a major effect on the dewatering process. A similar trend of pH value affecting sludge dewaterability has also been observed in other studies (Chen et al., 2001, Neyens and Baeyens, 2003) and the study of WAS in chapter 5.
6.3.3 Sludge digestibility

The BMP tests lasted for 36 d and the cumulative methane production of all testing groups is shown in Figure 6-3. The methane production from untreated PS was 410 ± 13 L/kg VS added. PS after treatments B - E ended up with a similar methane production about 370 ± 14 L/kg VS added, less than the control. The toxic metals were removed in the treatment F which achieved the highest production in all the treatments, 383 ± 2 L/kg VS added. The hydrolysis rate coefficient \((k)\) and biochemical methane potential \((B_0)\) of the anaerobic digestion process were estimated using first-order one-substrate model (Table 6-2) and the model fits are presented as lines in Figure 6-3. The \(k\) values of each of the groups were not significantly different \((p > 0.05)\).

The SCOD of PS after different treatments was presented in Table 6-2. The treatment by acidification led to no significant \((p > 0.05)\) change for SCOD. The addition of nitrite to both of those acidification methods did not cause considerable change for SCOD \((p > 0.05)\), either. The similar values of SCOD for all the samples can be one of the reasons for the similar \(k\) values for all the treatments.
Figure 6-3. Cumulative methane production from PS exposed to different treatments. Error bars show standard deviation from triplicate tests. The symbols represent the measured data and the lines represent the model fit.

Table 6-2. SCOD of PS after different treatment and estimated hydrolysis rate coefficient ($k$) and biochemical methane potential ($B_0$) of the AD process

<table>
<thead>
<tr>
<th>Treatment</th>
<th>SCOD (mg/L)$^a$</th>
<th>$k$ (d$^{-1}$)$^b$</th>
<th>$B_0$ (L CH$_4$/kg VS added)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Raw</td>
<td>$3437 \pm 308$</td>
<td>$0.30 \pm 0.05$</td>
<td>$401 \pm 14$</td>
</tr>
<tr>
<td>B: HCl acidification</td>
<td>$3630 \pm 52$</td>
<td>$0.34 \pm 0.07$</td>
<td>$358 \pm 16$</td>
</tr>
<tr>
<td>C: HCl acidification + nitrite</td>
<td>$3473 \pm 18$</td>
<td>$0.32 \pm 0.05$</td>
<td>$363 \pm 18$</td>
</tr>
<tr>
<td>D: ES acidification</td>
<td>$3952 \pm 166$</td>
<td>$0.27 \pm 0.05$</td>
<td>$368 \pm 20$</td>
</tr>
<tr>
<td>E: ES acidification + nitrite</td>
<td>$3880 \pm 140$</td>
<td>$0.27 \pm 0.05$</td>
<td>$365 \pm 20$</td>
</tr>
<tr>
<td>F: ES acidification + nitrite +</td>
<td>$3880 \pm 140$</td>
<td>$0.27 \pm 0.05$</td>
<td>$379 \pm 18$</td>
</tr>
<tr>
<td>metal removal</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: a. Average with standard deviation

b. Estimated value with 95% confidence intervals based on a two-tailed t-test in parameter standard errors
Generally, primary sludge is readily degradable so it is not as sensitive to treatments for digestibility improvement as waste activated sludge (Carrère et al., 2010). As presented above, a slight decrease of the methane production from PS through anaerobic digestion was caused by all the treatments. The same treatments, however, have been proven to be able to enhance the methane production from anaerobic digestion of WAS (chapter 5). The disruption of extracellular polymeric substance in WAS caused by the treatment was likely the reason for the improvement of its digestibility. Unlike WAS which is basically composed of bacterial cells, carbohydrates are the main part of PS (Gavala et al., 2003). Therefore, the treatment seemed to have no effect on increasing the digestibility of PS. However, the reason for the slightly inferior performance of methane production resulting from the treatment is still unclear and will need more investigation.

6.4 Conclusions

In this study, the effects of different treatments by acidification with nitrite addition on the toxic metal removal, digestibility and dewaterability of primary sludge were investigated, obtaining the following conclusions:

- The treatment by ES acidification with 10 mg NO$_2^-$-N/L nitrite for 5 h at pH 2 achieved the best efficiency of metal removal, 39 ± 1% and 82 ± 0.5% for Cu and Zn, respectively.

- All the treatments at pH 2 resulted in similar improvement for the dewaterability of primary sludge, increasing the dewatered sludge solids content from 29.8 ± 0.7% to 32.5 ± 1.0%.

- All the treatments at pH 2 made the methane production from anaerobic digestion of primary sludge slightly decreased, from 410 ± 13 L/kg VS added to 373 ± 13 L/kg VS added.
7. Implications for practice

7.1 Introduction

In the previous chapters, it was proven that nitrite addition to acidified sludge, either by HCl dosing or the electrochemical system (ES), had the ability to improve the sludge characteristics for beneficial reuse and disposal, *i.e.* toxic metal removal, pathogen reduction and enhancing sludge dewaterability and digestibility, simultaneously. Multiple benefits can be expected by using this novel technology for sludge treatment, giving potential for being economic feasible.

The main aim of this chapter is to evaluate the economic potential of the previously studied technology for practical application. The cost analysis was conducted for both HCl acidification and ES acidification. Disposal processes with and without anaerobic digestion (AD) were considered as two different scenarios. The costs introduced by the treatment processes and the benefits obtained from the achieved sludge characteristic improvement were compared to determine the economic potential.

7.2 Material and methods

7.2.1 Costs for the treatment processes

A wastewater treatment plant (WWTP) for 100,000 population equivalent (PE) was considered for the cost assessment, based on a dry sludge (DS) production of 80 g per capita per day (Hudson, 1995). The treatments were assumed to be conducted with sludge at 2.5% (w/w) total solids (TS).

The treatment conditions used in the calculation were fixed at the conditions used in chapter 5:

- **HCl treatment (acidification + nitrite + metal removal)**
  
  32% HCl for acidifying the sludge to pH 2;

  NaNO$_2$ dosing for a final concentration of 49 mg NaNO$_2$/L;

  NaOH for neutralisation and metal removal, the consumption was calculated based on moles of OH$^- =$ moles of H$^+$.  

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72


- **ES treatment (acidification + nitrite + metal removal)**

  The ES with a current efficiency (CE) of 85% for both anode and cathode processes, an operation cell voltage of 4.8 V and current density of 100 A/m², as achieved or observed on average in chapter 4 and 5;

  NaCl used for the electrolyte in the middle chamber and the consumption was calculated on the basis of moles of Cl⁻ = moles of Na⁺ = moles of e⁻ thought the circuit;

  NaNO₂ dosing for a final concentration of 49 mg NaNO₂/L;

  Neutralisation and metal removal would be achieved by the produced NaOH in the cathode and no extra alkali would be needed.

The initial Cu and Zn concentration was assumed at 437 mg Cu/kg DS and 687 mg Zn/kg DS, which are the average values observed in previous studies. The H⁺ consumption to achieve pH 2 sludge was based on the titration test in chapter 4.

Only the consumption of chemicals and electricity power were considered for the calculation of operational costs. The prices of the chemicals were from [http://www.alibaba.com](http://www.alibaba.com).

The capital cost was calculated based on Pikaar (2011), Rozendal *et al.* (2008) and Wang *et al.* (2013a). The prices of some of the material were from [http://www.alibaba.com](http://www.alibaba.com).

### 7.2.2 Benefits calculation

After the treatments, solubilised Cu and Zn were considered to be removed and the removal efficiency for Cu and Zn were the ones achieved in chapter 4 from which we selected the treatment condition. The improvement for sludge dewaterability and digestibility were selected as those achieved in chapter 5.

Two different scenarios were considered for the sludge disposal:

- **Direct disposal without AD**

  After the metal removal, the concentration of Cu and Zn were calculated for the treated sludge compared to NSW-EPA guidelines for classification and determination of corresponding disposal charge (Batstone *et al.*, 2011);
Sludge was assumed to be dewatered and the amount of wet sludge after dewatering was calculated based on the dewaterability achieved in chapter 5.

- **Disposal after 20 days of AD**

The treated sludge was assumed to go through continuous anaerobic digestion with a HRT of 20 days. Numerical uncertainty propagation method described by Batstone (2013) was adopted to estimate the methane production as the following procedures:

1) According to the outcomes of Chapter 5, one-substrate model (Equation 7-1) was used for untreated sludge (as control)

   \[ B(t) = B_0 \times (1 - \frac{1}{1+kt}) \quad (7-1) \]

   and two-substrate model (Equation 7-2) was used for HCl/ES treated sludge

   \[ B(t) = B_{0,\text{rapid}} \times (1 - \frac{1}{1+k_{\text{rapid}}t}) + B_{0,\text{slow}} \times (1 - \frac{1}{1+k_{\text{slow}}t}) \quad (7-2) \]

   Where the \( B(t) \) is cumulative methane yield at time \( t \) (L CH\(_4\) / kg VS added); the \( B_0 \) (\( B_{0,\text{rapid}} \) and \( B_{0,\text{slow}} \)) is biochemical methane potential (for rapidly and slowly degradable substrate, respectively); the \( k \) (\( k_{\text{rapid}} \) and \( k_{\text{slow}} \)) is hydrolysis rate coefficient (for rapidly and slowly degradable substrate, respectively) (d\(^{-1}\)); the \( t \) is time (d).

2) The values of the \( B_0, B_{0,\text{rapid}}, B_{0,\text{slow}}, k, k_{\text{rapid}} \) and \( k_{\text{slow}} \) and their standard deviation were from the parameter estimation in Chapter 5.

3) Apply pseudo-random sampling to calculate values for the \( B_0, B_{0,\text{rapid}}, B_{0,\text{slow}}, k, k_{\text{rapid}} \) and \( k_{\text{slow}} \).

4) Calculate the \( B(20) \) for the untreated sludge (control) using Equation 7-1 with 1,000 simulations and calculate the \( B(20) \) for the HCl/ES treated sludge using Equation 7-2 with 10,000 simulations according to Batstone (2013).

5) The average values of the \( B(20) \) from the simulations in previous step for each sludge were adopted as the methane production for the following calculation.

Heat and electric power would be generated from the combustion of produced methane with the conversion efficiency of 50% and 40%, respectively;
The VS destruction was calculated based on the methane production and equation 5-3;

Sludge reduction after AD was calculated based on the VS destruction;

The final concentrations of Cu and Zn were calculated according to the achieved metal removal and sludge reduction. Then the concentrations were compared to NSW-EPA guidelines for classification and determination of corresponding disposal charge (Batstone et al., 2011);

The digested sludge was assumed to be dewatered to a TS of 20% for disposal.

For both of the above two scenarios, the two different treatment processes were compared to the untreated sludge (control) in the aspects of disposal charge and power generation. Specific values for the above mentioned parameters are presented in the tables in the next section.

7.3 Results and discussion

7.3.1 Costs for the treatment processes

The annual sludge production from a WWTP for 100,000 PE was estimated as 2,920 t of dry solids. As sludge with 2.5% TS, the total volume of the produced sludge would be 116,800 t (m$^3$).

The total capital costs for treatments by HCl and ES acidification are presented in Table 7-1. An additional reactor for metal leaching would be needed. Due to the relatively short HRT of 5 h, the volume required for the metal leaching reactor was only 67 m$^3$, with a cost of AUD 70k (Wang et al., 2013a). Besides the metal leaching reactor, ES acidification would require another reactor for the electrochemical processes. With the demand of reactor, electrodes and membrane, the capital cost of the ES came up to AUD 672k. The total cost for the ES acidification with metal removal treatment was AUD 742k. It should be noted that the life time of reactor were assumed to be 25 years but 5 years for the electrodes and the membranes (Pikaar, 2011, Rozendal et al., 2008). As a result, cost for the replacement of membranes and electrodes every 5 years was also considered, with a total value of AUD 397k every 5 years.
Table 7-1 Capital cost for sludge treatment systems

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal leaching reactor</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HRT for leaching process</td>
<td>h</td>
<td>5&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Required leaching reactor volume</td>
<td>m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>67</td>
</tr>
<tr>
<td>Life time for reactor</td>
<td>year</td>
<td>25</td>
</tr>
<tr>
<td><strong>Cost for reactor</strong></td>
<td>AUD (k)</td>
<td>70&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>HRT for ES</td>
<td>h</td>
<td>2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Required ES reactor volume for anode</td>
<td>m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>27</td>
</tr>
<tr>
<td>Required ES reactor volume for other chambers</td>
<td>m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>10</td>
</tr>
<tr>
<td>Required electrode area</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>213&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Required membrane area</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>213&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Price of anode</td>
<td>AUD/m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1,250&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Cost for anode</strong></td>
<td>AUD (k)</td>
<td>267</td>
</tr>
<tr>
<td>Price of cathode (stainless steel mesh)</td>
<td>AUD/m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>10&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Cost for cathode</strong></td>
<td>AUD (k)</td>
<td>2</td>
</tr>
<tr>
<td>Price of membrane</td>
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<td>600&lt;sup&gt;e&lt;/sup&gt;</td>
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<td><strong>Cost of membrane</strong></td>
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<tr>
<td>Price for ES reactor</td>
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<td><strong>Cost for ES reactor</strong></td>
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<td>Price of others for ES reactor</td>
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<td>1,500&lt;sup&gt;e&lt;/sup&gt;</td>
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<tr>
<td><strong>Cost of other parts for ES reactor</strong></td>
<td>AUD (k)</td>
<td>55</td>
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<tr>
<td><strong>Cost for ES</strong></td>
<td>AUD (k)</td>
<td>672</td>
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</tbody>
</table>

Note:  

- a. Based on the results in chapter 4  
- b. According to Wang et al. (2013a), Cost = 497306 × (reactor volume / 1000)<sup>0.7202</sup>  
- c. According to Pikaar (2011)  
- d. From [http://www.alibaba.com](http://www.alibaba.com)  
- e. According to Rozendal et al. (2008)  

The total operational costs for the HCl treatment are presented in Table 7-2. The total annual costs reached AUD 281k, about 99% of which was contributed by the consumption of the acid and alkali.
Table 7-2  The annual cost for HCl treatment

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry sludge production</td>
<td>t</td>
<td>2,920</td>
</tr>
<tr>
<td>2.5% TS WAS production</td>
<td>t</td>
<td>116,800</td>
</tr>
<tr>
<td>H⁺ consumption rate</td>
<td>mol/t DS</td>
<td>2,282</td>
</tr>
<tr>
<td>32% HCl price</td>
<td>AUD/t</td>
<td>200</td>
</tr>
<tr>
<td>32% HCl consumption</td>
<td>t</td>
<td>758</td>
</tr>
<tr>
<td>Expense on 32% HCl</td>
<td>AUD (k)</td>
<td>152</td>
</tr>
<tr>
<td>NaOH price</td>
<td>AUD/t</td>
<td>400</td>
</tr>
<tr>
<td>NaOH consumption</td>
<td>t</td>
<td>267</td>
</tr>
<tr>
<td>Expense on NaOH</td>
<td>AUD (k)</td>
<td>107</td>
</tr>
<tr>
<td>HCl and NaOH storage</td>
<td>AUD (k)</td>
<td>20</td>
</tr>
<tr>
<td>NaNO₂ price</td>
<td>AUD/t</td>
<td>450</td>
</tr>
<tr>
<td>NaNO₂ concentration</td>
<td>mg/L</td>
<td>49</td>
</tr>
<tr>
<td>NaNO₂ consumption</td>
<td>t</td>
<td>5.8</td>
</tr>
<tr>
<td>Expense on NaNO₂</td>
<td>AUD (k)</td>
<td>3</td>
</tr>
<tr>
<td><strong>Total expense on treatment</strong></td>
<td>AUD (k)</td>
<td><strong>281</strong></td>
</tr>
</tbody>
</table>

As shown in Table 7-3, the annual operational cost for the ES treatment was AUD 191k, about 32% lower than that for the HCl treatment. The consumption of nitrite only contributed about 1.3% of the total cost. It was noticed that the cost of electricity for ES acidification was similar as the cost of the HCl for acidification. But the alkali produced in the cathode compartment of ES avoided the purchase of NaOH, which made a considerable difference between these two acidification methods. In addition, by using the ES acidification, WWTPs could also avoid the transporting, storing and handling of the corrosive concentrated acids and alkalis, as well as the serious occupational health and safety (OH&S) concerns associated with handling of these chemicals.
Table 7-3 The annual cost for treatment of ES acidification + metal removal

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry sludge production</td>
<td>t</td>
<td>2,920</td>
</tr>
<tr>
<td>2.5% TS WAS production</td>
<td>t</td>
<td>116,800</td>
</tr>
<tr>
<td>H⁺ consumption rate</td>
<td>mol / t DS</td>
<td>2,282</td>
</tr>
<tr>
<td>Faraday constant</td>
<td>A/mol</td>
<td>96,485</td>
</tr>
<tr>
<td>Current efficiency</td>
<td>%</td>
<td>85%</td>
</tr>
<tr>
<td>Quantity of electric charge needed</td>
<td>C</td>
<td>7.56 \times 10^{11}</td>
</tr>
<tr>
<td>Cell voltage</td>
<td>V</td>
<td>4.8</td>
</tr>
<tr>
<td>Electricity consumption</td>
<td>MWh</td>
<td>1,009</td>
</tr>
<tr>
<td>Electricity price</td>
<td>AUD/kwh</td>
<td>0.15</td>
</tr>
<tr>
<td>Expense on electricity</td>
<td>AUD (k)</td>
<td>151</td>
</tr>
<tr>
<td>NaCl price</td>
<td>AUD/t</td>
<td>80</td>
</tr>
<tr>
<td>NaCl consumption</td>
<td>t</td>
<td>459</td>
</tr>
<tr>
<td>Expense on NaCl</td>
<td>AUD (k)</td>
<td>37</td>
</tr>
<tr>
<td>NaNO₂ price</td>
<td>AUD/t</td>
<td>450</td>
</tr>
<tr>
<td>NaNO₂ concentration</td>
<td>mg/L</td>
<td>49</td>
</tr>
<tr>
<td>NaNO₂ consumption</td>
<td>t</td>
<td>5.8</td>
</tr>
<tr>
<td>Expense on NaNO₂</td>
<td>AUD (k)</td>
<td>3</td>
</tr>
<tr>
<td><strong>Total expense on treatment</strong></td>
<td>AUD (k)</td>
<td>191</td>
</tr>
</tbody>
</table>

7.3.2 Benefits from sludge treatment

7.3.2.1 Direct disposal without AD

The annual costs of direct sludge disposal and the total costs for the sludge management (the cost of sludge treatment + disposal) are presented in Table 7-4. The saving for the cost of sludge management were AUD 217k p.a. and AUD 337k p.a. for HCl and ES treatments, respectively. The benefits came mainly from two aspects:

- After the treatment, the dewaterability of sludge could be improved, resulting in higher total solids content after the dewatering process. The total amount of dewatered sludge for disposal was reduced from 20,000 t to 16,044 t and 15,450 t, respectively by the HCl and ES treatment.
Cu and Zn were removed from the sludge by the treatments, improving the sludge from Grade C to Grade B. So it is possible to dispose the sludge closer to urban areas rather than transport to remote agricultural areas, and more sludge could be applied to the available land without exceeding acceptable toxic metal concentrations in the soil. As a result, the average disposal charge could be reduced from AUD 65 per wet t to AUD 50 per wet t (Batstone et al., 2011). It should be noted that the ES treatment actually achieved a considerably lower residual metal concentration in the sludge than the HCl treatment, but this effect was not considered in the current calculations as both are achieving a sludge quality equivalent to Grade B. In some circumstances, the better metal removal of the ES treatment might create a further economic benefit due to higher land application rates.

**Table 7-4** Annual cost of direct sludge disposal without AD

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry sludge production</td>
<td>t</td>
<td>2,920</td>
</tr>
<tr>
<td>2.5% TS WAS production</td>
<td>t</td>
<td>116,800</td>
</tr>
<tr>
<td><strong>General</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Cu concentration</td>
<td>mg/kg DS</td>
<td>431</td>
</tr>
<tr>
<td>Initial Zn concentration</td>
<td>mg/kg DS</td>
<td>676</td>
</tr>
<tr>
<td>Grade C sludge disposal</td>
<td>AUD/wet t</td>
<td>65</td>
</tr>
<tr>
<td>Grade B sludge disposal</td>
<td>AUD/wet t</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TS after Dewatering</th>
<th>%</th>
<th>Control</th>
<th>HCl treatment</th>
<th>ES treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dewatered sludge production</td>
<td>t</td>
<td>20,000</td>
<td>16,044</td>
<td>15,450</td>
</tr>
<tr>
<td>Cu removal efficiency</td>
<td>%</td>
<td>0</td>
<td>26%</td>
<td>60%</td>
</tr>
<tr>
<td>Zn removal efficiency</td>
<td>%</td>
<td>0</td>
<td>65%</td>
<td>86%</td>
</tr>
</tbody>
</table>

| Specific                        |       |          |
|---------------------------------|-------|----------|---------------|
| Final Cu concentration          | mg/kg DS | 431     | 319           | 128          |
| Final Zn concentration          | mg/kg DS | 676     | 237           | 33           |
| Sludge classification           |       | Grade C | Grade B       | Grade B      |
| Disposal cost                   | AUD (k) | 1,300   | 802           | 772          |
| Cost for treatment              | AUD (k) | 0       | 281           | 191          |
| Total cost                      | AUD (k) | 1,300   | 1,083         | 963          |
| Saving                          | AUD (k) | 0       | 217           | 337          |
In this scenario, the total cumulative costs, including the capital and operation, for sludge management are presented in Figure 7-1. For the HCl treatment, net savings could be achieved from the 2nd year of the installation. But for the ES treatment, due to the relatively high capital cost, it would take 3 years to achieve break-even. After 11 years of operation, the total cost of the ES treatment becomes lower that the HCl treatment.

Figure 7-1 The cumulative cost for different sludge treatment over 25 years

The cost for sludge disposal plays a critical role on determining the final cost for sludge management. The treatments developed in this thesis improved the sludge quality, which reduced the disposal costs. To verify the feasibility of the treatments at different conditions, the saving from treatments (cumulative disposal cost of sludge with no treatment - cumulative cost of sludge with different treatments at 10 or 15 years of operation) was compared at different disposal costs for the sludge after the treatments (Figure 7-2). It was found that the net saving was quite sensitive to the change of disposal prices. For the HCl treatment, if the disposal price for the treated sludge is higher than AUD 62/wet t (AUD 3/wet t less than the disposal price of untreated sludge), there will be no saving gained from the treatment. For the treatment by the ES, as long as the price for the treated sludge disposal is less than AUD 64/wet t (AUD 1/wet t less than the disposal price of untreated sludge), a net saving can be achieved.
7.3.2.2 Disposal after Anaerobic Digestion

The annual costs for the sludge disposal after 20 days of AD are presented in Table 7-5. The amount of sludge for disposal was significantly reduced by the AD process. However, because of the sludge reduction during AD, the concentrations of toxic metals (expressed as mg/kg DS) actually increased for the control sludge. For the HCl treatment, 26% of Cu would be removed while the amount of solids was reduced by 32%, making the final Cu concentration higher than the initial value. As a result, the final sludge after AD was still classified as Grade C. The ES acidification performed much better in removing metals and achieved Grade B sludge after AD. So the cost for the final sludge disposal in this treatment was much lower.

The power production from burning the biogas produced from AD provides additional benefits. The comparison of the benefits (the capital cost for AD was not considered and it was assumed to be same for all the sludges) from the control group and the two different treatments is presented in Table 7-6. It was noticed that due to the cost of chemicals consumed in the treatment process, the treatment by HCl made the disposal more expensive than the control group, which made the HCl treatment not economically attractive in this scenario. But the treatment by the ES was able to achieve large savings in total cost (AUD 185k p.a., Table 7-6) compared with the disposal of the digested sludge without treatment.
Table 7-5  Annual cost for sludge disposal after AD

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry sludge production</td>
<td>t</td>
<td>2,920</td>
</tr>
<tr>
<td>2.5% TS WAS production</td>
<td>t</td>
<td>116,800</td>
</tr>
<tr>
<td>Sludge TS/VS ratio</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>Initial Cu concentration</td>
<td>mg/kg DS</td>
<td>437</td>
</tr>
<tr>
<td>Initial Zn concentration</td>
<td>mg/kg DS</td>
<td>683</td>
</tr>
<tr>
<td>Grade C sludge disposal</td>
<td>AUD/wet t</td>
<td>65</td>
</tr>
<tr>
<td>Grade B sludge disposal</td>
<td>AUD/wet t</td>
<td>50</td>
</tr>
<tr>
<td>TS of dewatered digested sludge</td>
<td>%</td>
<td>20%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Control</th>
<th>HCl treatment</th>
<th>ES treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS destruction</td>
<td>%</td>
<td>33.6%</td>
<td>41.0%</td>
<td>41.8%</td>
</tr>
<tr>
<td>Solids residue after AD</td>
<td>t</td>
<td>2,165</td>
<td>1,999</td>
<td>1,981</td>
</tr>
<tr>
<td>Digested sludge production</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(dewatered)</td>
<td>t</td>
<td>10,826</td>
<td>9,995</td>
<td>9,906</td>
</tr>
<tr>
<td>Cu removal efficiency</td>
<td>%</td>
<td>0</td>
<td>26%</td>
<td>60%</td>
</tr>
<tr>
<td>Zn removal efficiency</td>
<td>%</td>
<td>0</td>
<td>65%</td>
<td>86%</td>
</tr>
<tr>
<td>Final Cu concentration</td>
<td>mg/kg DS</td>
<td>631</td>
<td>525</td>
<td>291</td>
</tr>
<tr>
<td>Final Zn concentration</td>
<td>mg/kg DS</td>
<td>986</td>
<td>388</td>
<td>159</td>
</tr>
<tr>
<td>Sludge grade</td>
<td></td>
<td>Grade C</td>
<td>Grade C</td>
<td>Grade B</td>
</tr>
<tr>
<td>Dewatered sludge disposal cost</td>
<td>AUD (k)</td>
<td>704</td>
<td>650</td>
<td>495</td>
</tr>
</tbody>
</table>
Table 7-6  Power generation from AD of sludge after different treatment

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry sludge production</td>
<td>t</td>
<td>2,920</td>
</tr>
<tr>
<td>Sludge TS/VS ration</td>
<td>-</td>
<td>1.3</td>
</tr>
<tr>
<td>Initial VS</td>
<td>t</td>
<td>89,846</td>
</tr>
<tr>
<td>Power price</td>
<td>AUD/kWh</td>
<td>0.15</td>
</tr>
<tr>
<td>Methane calorific value</td>
<td>kWh/kg CH₄</td>
<td>16</td>
</tr>
<tr>
<td>Gas molar volume</td>
<td>L/mol</td>
<td>22.4</td>
</tr>
<tr>
<td>CH₄ molar mass</td>
<td>g/mol</td>
<td>16</td>
</tr>
<tr>
<td>Conversion efficiency of methane to heat</td>
<td>%</td>
<td>50%</td>
</tr>
<tr>
<td>Conversion efficiency of methane to power</td>
<td>%</td>
<td>40%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Control</th>
<th>HCl treatment</th>
<th>ES treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ production rate</td>
<td>L/ kg VS</td>
<td>199</td>
<td>245</td>
</tr>
<tr>
<td>Methane production</td>
<td>t</td>
<td>320</td>
<td>393</td>
</tr>
<tr>
<td>Heat production</td>
<td>MWh</td>
<td>2,559</td>
<td>3,142</td>
</tr>
<tr>
<td>Electricity production</td>
<td>MWh</td>
<td>2,047</td>
<td>2,514</td>
</tr>
<tr>
<td>Benefits from power</td>
<td>AUD (k)</td>
<td>691</td>
<td>848</td>
</tr>
<tr>
<td>Treatment costs</td>
<td>AUD (k)</td>
<td>0</td>
<td>281</td>
</tr>
<tr>
<td>Disposal costs</td>
<td>AUD (k)</td>
<td>704</td>
<td>650</td>
</tr>
<tr>
<td>Net benefits</td>
<td>AUD (k)</td>
<td>-13</td>
<td>-82</td>
</tr>
</tbody>
</table>

In Figure 7-3, the net benefits made by AD of the untreated sludge and the ES treated sludge were compared. The treatment by the HCl was not considered in this comparison because it will generate even less benefit than the untreated sludge. For the treatment by the ES acidification, even with the high initial capital cost, a net benefit was achieved from the 7th year after installation.
The additional methane production from will increase the relative mineral contents of digested sludge, from which a better dewatering characteristic can be expected (Kopp et al., 1997). As a result, the final production of dewatered sludge after AD can be reduced further, giving more benefits for sludge management. Different HRTs of AD will lead to different biogas production and sludge reduction. The additional benefits (over 15 years of operation) from the ES treatment at different AD HRTs and dewatered sludge solids concentrations (% TS) are plotted in Figure 7-4. It was discovered that the HRT of AD would not have a huge effect on the saving from the ES treatment. The change of HRT from 15 d to 25 d would only increase the savings by about AUD 0.2 - 0.3 million. But the digester volume needs to be increased by 67%, introducing corresponding increase for capital investment and the operation of the digester (e.g. more mixing energy). Therefore, shorter HRT of AD might be more economic when the capital cost of digester is also taken into consideration. The sludge dewaterability greatly affected the obtained net benefit from the sludge treatment by the ES. The change of solids content of dewatered sludge from 20% to 26% increased the achievable benefit by about 3 times.

**Figure 7-3** The cumulative net benefit from sludge after different treatment
Figure 7-4 Additional benefits from ES treatment with different HRT of AD and solids content of dewatered sludge

7.4 Conclusions

Based on the sludge treatment conditions and achieved sludge characteristics described in chapters 3, 4 and 5, the cost analysis was conducted to evaluate the economic feasibility of the sludge treatments by the HCl/ES acidification with nitrite and metal removal, with the following conclusions obtained:

- For direct sludge disposal without AD: the HCl treatment achieved net savings for sludge disposal from the 2nd year of installation; the ES treatment achieved the break-even point in the 4th year after installation and out-performed the HCl acidification from the 11th year.

- For the sludge disposal after AD: the ES treatment achieved significant operational benefits compared to no sludge treatment. However, it would take about 7 years to repay the capital costs. The HRT of AD would not affect the economic potential very much but the increase of dewaterability of digested sludge would substantially improve the benefits.
8. Conclusions and recommendations

This thesis successfully developed a novel technology concept for sludge treatment, achieving enhanced toxic metal removal, pathogen reduction, sludge digestibility and dewaterability at the same time. In this chapter, the main conclusions and findings from the research are summarised, with the highlights of the significance and implication as well as the recommendations for future studies.

8.1 Conclusions

8.1.1 Toxic metal removal

- Using a nitrite addition of 20 mg NO$_2^-$-N/L, the removal of Cu from acidified (pH 2) WAS was improved from 3 - 7% to 45 - 64% and for Zn from about 70% to > 80%.

- The improvement of Cu and Zn removal from WAS mainly resulted from the substantially increased solubilisation of organically bound Cu and Zn as a consequence of the nitrite addition.

- Nitrite addition at 10 mg NO$_2^-$-N/L and a treatment time of 5 h at pH 2 were found to be the optimised condition for enhancing metal removal.

- WAS acidification by *in situ* electrochemical acid production followed by the optimised nitrite treatment achieved superior Cu and Zn removal compared to the treatment with external acid dosing, reaching 60 ± 2% Cu and 86 ± 1% Zn solubilisation.

- For primary sludge (PS), only the electrochemical acidification followed by optimised nitrite treatment achieved a significant metal removal (39 ± 1% for Cu and 82 ± 0.5% for Zn).

8.1.2 Enhancement of sludge digestibility

- The optimised treatment (using HCl acidification) followed by metal removal significantly enhanced WAS digestibility, increasing methane production by 46 ± 3% after 69 d of batch BMP tests.
Electrochemical acidification with the optimised treatment led to even better WAS digestibility. The methane production was increased by $55 \pm 6\%$ during a 69 d batch BMP tests. The VS destruction in the same test increased from 42\% to 65\% compared to the untreated WAS.

Only a minor effect of the acid/nitrite treatment on the PS digestibility was observed.

### 8.1.3 Enhancement of sludge dewaterability

For WAS, all the treatments at pH 2 (either acidified by acid dosing or electrochemical acid generation) increased the dewaterability of sludge. Using a proxy belt filter dewatering test, the solids content of dewatered WAS after treatment was $18.9 \pm 0.7\%$, compared with $14.6 \pm 0.7\%$ for untreated WAS. The addition of nitrite did not affect WAS dewaterability.

For PS, all the treatment at pH 2, with and without nitrite, did not affect sludge dewaterability, achieving a dewatered sludge solids content of $32.5 \pm 1.0\%$ compared with $29.8 \pm 0.7\%$ for untreated PS.

### 8.1.4 Pathogen reduction

The concentration of pathogen indicators, total coliforms and *E.coli*, in WAS was reduced from the level of $10^7$ and $10^6$ MPN/kg DS to $10^4$ and $10^4$ MPN/kg DS, respectively, by the treatment at pH 2. The addition of 10 mg NO$_2$-N/L during sludge treatment reduced the concentration of total coliform and *E.coli* further by one to two orders of magnitude (log reduction). Overall, the combined treatment achieved about 4 log (99.99\%) reductions for both pathogen indicators, which is a major benefit of the process.

### 8.1.5 Economic analysis

For the sludge management without AD, the acid/nitrite treatment could upgrade the sludge quality from Grade C to Grade B by removing toxic metals and reduce the sludge volume by increasing sludge dewaterability, from which net savings on sludge disposal cost could be achieved.

For the sludge management with AD, net saving on sludge disposal cost could be achieved from the extra biogas production and sludge volume reduction introduced by the enhanced sludge digestibility after the ES acidification/nitrite and metal removal treatment.
8.2 Significance and implications of the research findings

Sludge management is a critical issue for wastewater utilities. The organic matter and nutrient content in the wastewater sludge provide the potential of beneficial reuse, including energy and resource recovery. Typically, the sludge characteristics need to be improved through a range of treatment options before beneficial reuse to minimise any possible negative effects to the environment and maximise the beneficial outcomes. However, the application of sludge treatment is often limited by the poor balance between the costs and benefits introduced by the treatment. The novel technology concept developed in this thesis is able to gain significant improvements for multiple sludge characteristics. The cost analysis in chapter 7 clearly indicates the great potential for gaining a net benefit from the novel sludge treatment technology by achieving higher sludge quality and lower sludge quantity. Two scenarios, with and without AD, were considered. Both of them were proven to have good potential of being economically attractive, indicating the general applicability of this technology for different wastewater treatment processes and different WWTP sizes. The HRT of the developed technology was only 5 - 7 h so the capital costs can be controlled at a relatively low level, while the operating costs are largely due to acid and alkali (or electricity) addition, the costs of which are quite predictable. Using the in situ electrochemical sludge acidification and alkali production has the added benefit that it avoids the handling and the OH&S issues relating to the use of corrosive/dangerous chemicals. All of the above give a promising potential for the application of this novel technology. It should be noted that the capital cost and the longevity of ES is still unknown and will require follow-up pilot (scale-up) studies for further evaluation.

Nitrite was introduced for the first time to enhance the toxic metal removal from sludge. By the analysis of metal distribution through SCE, it was found that the difficulty of efficient removal of metals was due to the resistance to acid leaching of organically bound metals, especially for Cu. Advanced oxidation by Fenton reaction can enhance the metal removal but requires dosing of more than 10 g H₂O₂/kg DS as well as ferrous ions (e.g. FeSO₄) (Dewil et al., 2007, Ito et al., 2008, Neyens et al., 2003). The dosage of nitrite in this thesis was only about 2 g of NaNO₂/kg DS, whilst already achieving comparable metal removal efficiency. Besides, the H₂O₂ is unstable and corrosive so its handling requires more attention and effort compared to NaNO₂. In this aspect, nitrite treatment shows major advantages over Fenton oxidation for sludge treatment. The nitrite also significantly improved the digestibility of the sludge. For both effects, the formation of free nitrous acid (FNA) at the pH 2 was believed to be the actual factor. Given the critical role of EPS in sludge for metal binding and AD resistance, the outcomes in this thesis provide indications for the
disruption of EPS by nitrite or FNA, which is valuable for fundamental study of working mechanism of nitrite or FNA to sludge.

The results in chapter 4 showed that the acidification by ES led to much higher metal removal than that achieved by acid (HCl) dosing, with the reasons believed to be the oxidation of sludge by agents produced at the anode (e.g. free chlorine and OH·). Similarly, the improvement of the sludge digestibility after anodic acidification was greater than after acid dosing. The sludge treatment involving in situ electrochemical sludge acidification and alkali generation not only avoids the handling of corrosive chemicals but also provides better performance. As acid and alkali are commonly used chemicals for wastewater utilities, the in situ production of acid and alkali by ES from sludge or sludge liquor achieved in this thesis is expected to be of great use.

Unlike most previous studies that focused on investigating the metal removal from digested sludge (Babel and del Mundo Dacera, 2006, Pathak et al., 2009), the treatment concept developed in this thesis was applied to (fresh) WAS and PS. Since AD is not always available at all WWTPs, especially small scale ones, the treatment developed in this thesis for undigested sludge would be more generally applicable. More importantly, the treatment also improved the AD performance. Most of the pretreatments for enhancing AD function by increasing sludge solubilisation (Carrère et al., 2010). In this thesis, the treatment only solubilised a maximum of 7% of TCOD but achieved up to 55% increase of methane production and 65% of VS destruction, indicating that the treatment mainly affected the solid fraction of sludge. High-solids AD is operated at solids content higher than 20 wt% and has many advantages over conventional AD, such as smaller reactor size and lower operation costs (Duan et al., 2012, Guendouz et al., 2008, Hartmann and Ahring, 2006). The combination of the treatment in this thesis and high-solids AD might be an alternative option, especially for smaller size WWTPs. After the treatment, the energy potential would still be maintained mostly in the solids and the improved digestibility of solids guarantees higher methane production. The increased dewaterability also reduced the solids volume for handling.

Toxic metals are inhibitors for AD (Chen et al., 2008). However, not much attention is paid on removing toxic metals to improve AD. In this thesis, it was found that even at low concentrations of metals, the removal of Cu (from about 10 mg/L to about 4 mg/L) and Zn (from about 16 mg/L to about 2 mg/L) had a significant positive effect on the performance of AD. These small reductions in metal concentrations had a significant effect in enhancing the production of about 40 L CH₄/kg VS, hence suggesting that methane production is inhibited in AD at quite low metal concentrations.
8.3 Recommendations for future studies

8.3.1 Move to practical application

This thesis demonstrated the technical feasibility of achieving multiple benefits for sludge management through a simple acid/nitrite sludge treatment. The economic potential was also proven through the cost analysis. For a full scale practical application of this sludge treatment technology, several aspects require further studies:

- The optimised conditions for sludge treatment in this thesis were determined according to the performance of metal removal. The pathogen reduction by the treatment at this condition was good but still slightly insufficient to meet stabilisation Grade A. In addition, the sludge digestibility could potentially be further enhanced at different treatment conditions. As a result, the treatment parameters still need to be further optimised, depending on which sludge characteristic(s) is (are) most critical, the availability of resources and the cost-effectiveness. The parameters that can be manipulated include: pH, nitrite concentration (ratio between sludge TS or VS to NO$_2^-$-N), exposure time, anodic process duration and so on.

- The cost analysis in this thesis was based on the experimental outcomes from laboratory scale batch tests. Only the costs of chemical and electricity consumption and the estimated capital costs were considered. The biogas production and sludge reduction from AD were calculated from the parameter ($B_0$ and $k$) estimation through a first-order kinetic model. The acid/nitrite treatment was able to enhance the removal of metals. Meanwhile, the simultaneously increased sludge digestibility also reduced the amount of dry solids after AD. Considering the concentration of metal in sludge is typically evaluated in the form of mg metal per kg dry solids, whether the metal concentration will be increased or decreased after acid/nitrite treatment and AD still requires further study. In addition, the enhanced digestibility and higher VS destruction would increase the relative mineral content, which potentially could further improve the sludge dewaterability after AD (Kopp et al., 1997), but needs to be further studied at a larger scale. For practical applications, a long-term pilot-scale study is needed for further investigations of the challenges and benefits, and the economic feasibility of this technology.

- The electrode employed in the anodic process was IrO$_x$ coated Ti mesh. The life time of the coating and the cost of this kind of electrode are critical for the practical application. Studies on the performance of cheaper electrode materials would be valuable before implementation.
In this thesis, the data from 3 different WWTPs showed good consistency and strong agreement that the acid/nitrite treatment significantly enhanced the removal of Cu and Zn, which were commonly reported as the problematic metals in sludge (Babel and del Mundo Dacera, 2006, Pritchard et al., 2010). Still, the study of the effect of acid/nitrite treatment on solubilising some other metals, such as Cd, Cr, Pb and so on, would be recommended to further prove the general applicability and potential additional benefits of this technology.

Resource recovery is increasingly critical for developing a sustainable sludge management strategy. It has been estimated that the value of metals in sludge could approach up to $460/ton DS (Westerhoff et al., 2015). Using the novel treatment method, metals can be solubilised and removed from sludge. The recovery, or even differential recovery, of solubilised metals would be of great interest for researching and may provide extra benefits to the whole sludge management. However, how to recover them effectively (maybe electrochemically or biologically) and how to achieve net cost benefits would need further study.

The acid/nitrite treatment was proven to be effective for metal removal and pathogen reduction. Another factor limiting sludge land application is the concentration of organic contaminants. How the acid/nitrite treatment will affect on organic contaminants is also worth studying, especially for the electrochemical acid generation process where chlorine formation might be an important side reaction.

8.3.2 Reveal of the working mechanism of nitrite and anodic process on sludge

The release of organically bound metals and the enhanced sludge digestibility provided strong indications for the effect of acid/nitrite treatment on sludge EPS. However, the underlying processes during the treatment are still unclear. The study of how nitrite or FNA affects sludge EPS and how the anodic process contributes to metal removal and digestibility enhancement would be very valuable.


USEPA (1992) Standards for the use or disposal of sewage sludge.


