Department of Chemical Engineering

Faculty of Science and Engineering

Conditioning and Dewatering of Anaerobically Digested Sludge from Municipal Wastewater Treatment Processes

Lau Shiew Wei

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: ………………………………………………

Date: ………26 November 2015………………

DEDICATION

We are made the stewards of the Earth.
Be it clean water or dirty water,
use it and dispose it wisely.

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PUBLICATIONS

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ABSTRACT

The wastewater treatment operations have constantly experienced revolutions for better handling and management of sludge. Anaerobic digestion and sludge dewatering are two critical processing units in sludge treatment which have drawn considerable research interests in order to accelerate the digestion process to stabilise the sludge without failing the subsequent dewatering performance. Anaerobically digested sludge is generally conditioned prior to dewatering due to the colloidal and compressible nature of sludge which causes poor dewaterability. Various sludge conditioning methods in the form of chemical, physical or biological treatment have been applied to alter the sludge properties such as the surface charge, the particle size, the particle mass density, and the floc structure, to enhance water removal.

The purpose of this thesis was to investigate the dewatering performance improvement of digested biological sludge with novel application and assessment of conditioning aids. The effectiveness of sludge conditioning was evaluated by batch experiments using a series of 250-mL jar test beakers to simulate a mixing, flocculation, and settling cycle. Dosage and type of conditioner, pH, temperature, mixing speed and mixing time were studied for their effects on sludge conditioning and dewatering. The sludge dewaterability was assessed by capillary suction time (CST), turbidity, electrical conductivity, zeta potential, cake solids content and particle size. Fourier Transform Infrared spectrum and microscopic imaging were applied to examine the chemical interaction and floc structure respectively. Data performed on synthetic sludge were compared to control data from anaerobic digested sludge in selected parameters. Additionally, the rheological rotational tests were carried out in controlled shear rate mode to study the sludge rheological behaviour and its application in optimisation of chemical dosage.

Results show that the low molecular weight chitosan was effective in water removal at even very low dosage but higher dosage formed bulky sludge flocs with more trapped water. Increase in chitosan dosage increased sludge dewaterability and enhanced sludge resistance to flow and network strength. From the sludge dewaterability studies, the optimal dosage was found at the range of 15–20 g/kg

chitosan where the values of CST, turbidity and cake solids content were attained between 6.6–11.0 s, 35.4–40.6 NTU and 24.3–25.3% respectively. In terms of sludge rheology, the conditioning dosage of 20 g/kg showed much improved rheological behaviour than the one at 15 g/kg with increased high-shear viscosity, yield stress and peak height in the rheogram, recorded as 38.0 mPa.s, 7.40 Pa and 11.41 Pa respectively.

The role of various cationic polymers and inorganic conditioning materials on anaerobic digested sludge and synthetic sludge has been tested in this study. The presence of increased cationic charges from the trivalent inorganic cations enabled extensive network bridging and gave effective destabilisation and sludge flocculation. Similarly, the cationic polymers effectively dewatered sludge via charge neutralisation and polymer bridging which aided the flocculation of sludge. However inorganic chemicals exhibited favourable network strength of one to two orders higher than the ones of cationic polymers.

On the other hand, acid treatment (lowering pH) and alkaline treatment (increasing pH) in sludge conditioning enhanced the release of bound water into free water to different extent as a result of the possible cell disruption and desorption of extracellular polymeric substances. Low pH was found most favourable for sludge conditioning in this study as it further enhanced the ionisation of the amine groups of organic polymers and suppressed the negative surface charges carried by the sludge particles. Conditioning temperature had a minor effect on sludge dewatering performance. The mixing effect was found less significant as well although restabilisation occurred with increasing mixing speed and mixing time during the flocculation step.

Studies of sludge rheology reveal that the synthetic sludge exhibited non-Newtonian pseudoplastic flow behaviour. It was satisfactorily modelled by the power-law model with high confidence, in agreement with most of the digested sludge behaviours found in the literature. When conditioned with chitosan, only sludge sampled from the fluid phase exhibited an excellent fit of the Bingham model. The rheological properties of suspended sludge and settled sludge after conditioning were difficult to model with the commonly known sludge models as the polymer-sludge network strength was disrupted and broken into smaller units of flocculated spheres under shear. However, it was found that the rheological properties (i.e., high-shear viscosity, yield stress and rheogram peak value) correlated well to the sludge dewaterability parameter under the different physicochemical parameters. Rheology can be used as a tool to optimise the chemical dosage in sludge conditioning and dewatering when used in conjunction with sludge dewaterability parameter. Optimisation using the response surface method suggests that the change in pH gave more impact to sludge dewaterability compared to the dosage effect, and the effect of temperature was insignificant. The optimal process settings were predicted at the dosage of 20 g/kg and pH 4 within the factorial range applied.

Meanwhile the dual-chemical conditioning results indicate a higher rate of water removal at the expense of dry solids content compared with single conditioning. The compound use of chitosan polymer and inorganic metal cation in dual-conditioning enhanced the sludge dewatering performance via the proposed joint effects of charge neutralisation coupled with double layer compression, salting out effect with cell disruption and bridging of the colloidal particles. It is thus feasible to supplement the nontoxic biopolymer chitosan with some cheaper inorganic chemicals in sludge conditioning to achieve a satisfactory degree of water removal for a more economical and sustainable sludge management.

Keywords: Anaerobic digestion, sludge conditioning, sludge dewatering, rheology, chitosan

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NOMENCLATURE

Symbols

$\dot{\gamma}$	Shear rate (s^{-1})
η	Dynamic viscosity (kg/m.s or Pa.s)
η_0	Low-shear or zero shear viscosity (kg/m.s or Pa.s)
η_∞	High-shear or infinite shear viscosity (kg/m.s or Pa.s)
η_L	Limit viscosity (kg/m.s or Pa.s)
τ	Shear stress (Pa)
τ_0	Yield stress (Pa)
ΔP	Applied vacuum pressure (N/m^2)
A	Filtration area (m^2)
b	Coefficient in Specific Resistance to Filtration equation (s/m^6)
C_C	Conditioner concentration (g/L)
D_C	Desired dosage (g/kg)
E_a	Activation energy (J/mol)
F	Temperature correction factor in Specific Gravity equation
K	Empirical constant in Arrhenius equation
K	Consistency index in rheology
m	Shear thinning or flow behaviour index
n	Number of dilution
R	Universal gas constant (J/mol.K)
R	Weight of water at 4°C in Specific Gravity equation (g)
S	Weight of sludge sample and cylinder in Specific Gravity equation (g)
T	Absolute temperature (K)
T	Calibrated turbidity (NTU)
t	Time of filtration (s)
T_0	Turbidity after dilution (NTU)
TS	Total solids of sludge (g/L)
TS_0	Total solids of sludge before dilution (g/L)

TS_S	Total solids of supernatant (g/L)
V	Volume of filtrate (m^3)
V, V_s	Volume of sludge sample (mL)
V_0	Volume of sludge before dilution
V_C	Dosing volume of conditioner (mL)
W	Weight of dried residue and dish or filter paper (g)
W	Weight of empty cylinder in Specific Gravity equation (g)
W_0	Weight of empty dish or filter paper (g)
w	Weight of dry cake per unit volume of total filtrate collected (kg/m^3)
w/w	Weight/weight

Abbreviations

3D-EEM	Three dimensional excitation emission matrix
AD	Anaerobic digestion, anaerobically or anaerobic digested
ADS	Anaerobic digested sludge
ANOVA	Analysis of variance
APHA	American Public Health Association
AS	Activated sludge
ATP	Adenosine triphosphate
ATR	Attenuated Total Reflectance
AWWA	American Water Works Association
BOD	Biochemical oxygen demand
CCD	Central composite design
COD	Chemical oxygen demand
cPAM	Cationic polyacrylamide
CST	Capillary suction time
DAFT	Dissolved air flotation thickening
DCB	Divalent Cation Bridging

DLVO	Derjaguin-Landau-Verwey-Overbeek
DNA	Deoxyribonucleic acid
EC	Electrical conductivity
EPS	Extracellular polymeric substances
FTIR	Fourier Transform Infrared
M/D	Monovalent to divalent
MW	Molecular weight
NTU	Nephelometric Turbidity Unit
PAM	Polyacrylamide
PRESS	Predicted residual sum of squares
PS	Primary sludge
RSM	Response surface method
SEM	Scanning electron microscope
SG	Specific gravity
SOP	Standard Operating Procedure
SRF	Specific resistance to filtration
SS	Secondary sludge
TDS	Total dissolved solids
TS	Total solids
TSS	Total suspended solids
TTF	Time to filter
USEPA	United States Environmental Protection Agency
VSS	Volatile suspended solids
WEF	Water Environment Federation
WWTP	Wastewater treatment plant
ZP	Zeta potential

CHAPTER 1

INTRODUCTION

In recent years, anaerobic digestion (AD) has been used widely as an attractive technology for sludge reduction and stabilisation but the resulting digested sludge is typically of poor dewaterability. It is commonly agreed that sludge dewatering is a bottleneck in the operation of municipal wastewater treatment plants (WWTPs), considering the colloidal and gel-like nature of sludge (Luo et al. 2015). Sludge management alone may contribute to almost half of the total wastewater treatment costs in terms of manpower, energy and unit processes which pose a great challenge for engineers and scientists. With increasing awareness of sustainable sludge management for WWTPs, AD and sludge dewatering have drawn considerable research interests in order to accelerate AD without failing the subsequent dewatering performance. The intricate nature of sludge characteristics which change instantly with time, temperature and its surrounding environment make it impossible to carry out controlled experiments in sludge studies. To address this issue, a good understanding of sludge behaviour is vital to improve and optimise the current state of WWTP operation. Systematic assessment of sludge dewaterability and rheology with the addition of conditioners in a distinct sludge system is expected to give valuable inputs to the development of sludge handling research.

1.1 Background and Problem Statement

Sewage sludge production has increased dramatically during the last few decades due to increased urban and industrial water purification activities (Saveyn et al. 2005). Appels et al. (2008) reported that the European Union produced nearly 10 million tons of dry sludge per year based on the calculation of 60 to 90 g dry solids per population equivalent per day. The large amount of sludge handling is an expensive process which may represent up to 40% of the capital cost and 50% of the operation cost of a WWTP (Spellman 2009). In addition to the economic burden, WWTPs are also facing strict sludge handling and management rules and regulations imposed by various state and federal governmental environmental protection agencies. In the United States (U.S.), as early as 1993, the U.S. Environmental Protection Agency (USEPA) had established the pollutant numerical limits and management practices for the reuse and disposal of solids generated from the wastewater processing units in the regulations addressed by 40 CRF Part 503 (Sewage Sludge Regulations) (Metcalf and Eddy 2003). The continuous challenge for many municipal agencies is to process sludge in a sustainable way while conserving both the environment and public health.

The high water content along with the colloidal and compressible nature of sludge, particularly the activated sludge and digested sludge, makes its handling and processing extremely costly in terms of both money and time. After gravitational thickening, sewage sludge still contains only as little as about 1–5% (*w/w*) of dry matter, the remaining fraction being water (Saveyn et al. 2005). The nature of sludge is complex with wide variation in its physical, chemical and biological properties. Sludges are produced from various sources in a WWTP such as primary treatment sludge, secondary treatment sludge and anaerobic digested (AD) sludge. Sludge contains free water and bound water. Free water can be easily removed whereas bound water is difficult to remove and hence requires effective conditioning aids and dewatering process.

AD has been practised in many WWTPs to stabilise organic matters in favour of its bioenergy production. The economic performance of an AD system depends on dewatering process which is the removal of water fraction from biosolids. Digested sludge is generally conditioned prior to dewatering due to the colloidal and compressible nature of the sludge which hampers its dewatering. Research evidence however suggests that AD of sludge leads to poorer dewatering characteristics due to increase in soluble proteins and polysaccharides (Novak 2010, Novak et al. 2003). This may result in high quantity of conditioning requirements, lower quality of final processed biosolids, and consequently higher operation and disposal costs. Until recently, there has been little published information on the dewaterability of digested sludge and the influencing factors of sludge dewaterability aided by emerging conditioning compounds. Dewatering is still a bottleneck for sludge treatment especially those that involve AD and it is specific for a WWTP.

Sludge may be pre-treated or conditioned by biological, chemical, and/or physical treatment to enhance dewaterability. To enhance the dewatering process performance, various chemical conditioning agents including high molecular weight polymeric compounds are widely used. This addition of the polymeric compounds enhances the aggregation of the colloidal particles, originally present in the pre-treated sludge into large dense flocs which settle in solution. Cationic polymers are the most widely used polymers for sludge since most sludge solids carry negative charges due to the presence of extracellular polymeric substances (EPS) (Chitikela and Dentel 1998, Mikkelsen and Keiding 2002). Recently there has been considerable interest in using alternative substances such as plant-based coagulants, soy and wheat proteins, surfactants, enzymes, natural or modified biopolymers, microbial flocculants, seawater and brine, to replace or to supplement synthetic polymers in sludge conditioning due to the high polymer costs, the high moisture content in the resulting sludge cake, and the concern over biodegradation and toxicity of polymers (Banerjee 2014, Liu et al. 2012, Liu et al. 2011, Prado et al. 2011a, b, Yin 2010, Fu et al. 2010, Zhang et al. 2010, Ayol 2005, Huang et al. 2002, Chen et al. 2001, Wang et al. 2014, Kuutti et al. 2011). One of the potential polymeric compounds–chitosan has unique properties among biopolymers due to the presence of primary amino groups which make it the only pseudo-natural cationic polymer (Rinaudo 2006, Renault et al. 2009). The application of chitosan in water and wastewater treatment is well recognised. For sludge application, chitosan has been studied in general for sludge flocculation by examining the turbidity and zeta potential values but the specific measurements with respect to sludge dewaterability such as capillary suction time (CST) and sludge rheological properties have not been explored in depth (Kaseamchochoung et al. 2006).

On the other hand, dual-chemical conditioning and dewatering has been proposed as an alternative to either lower the cost using a less expensive inorganic conditioner for part of the chemical usage or improve dewaterability through combination of chemicals (Kuglarz et al. 2008, Ozkan and Yekeler 2004, Lee and Liu 2001, 2000, Chitikela and Dentel 1998). Combining these two factors, it is hypothetical that dual-conditioning of sludge using the nontoxic and biodegradable biopolymer such as chitosan to replace synthetic polymers, combined with some cheaper metal cations may serve as an economical and eco-friendly novel dewatering alternative and hence this study was undertaken. The concept of dual-conditioning is based on the hypothesis that the destabilisation can be accomplished by elimination of charge barrier through the addition of cations. This allows small flocs to form; at the same time, the polymer bridging action serves to link these into substantially larger units with polymer addition. The addition of cations could supplement the more expensive polymer and neutralise a portion of the negative charge and/or introduce additional binding (for multivalent cations) in the sludge system. Although there have been much data on the dewatering behaviour of sludge when conditioned with either cationic polymers or cations, there have not been any detailed studies on the effect of cation addition on sludge dewatering when used in conjunction with polymers or polyelectrolytes in the literature. The mechanisms governing the different dewatering performances of cations are not well understood, although they should be highly related to the physicochemical properties of sludge and the simultaneous interactions between sludge and dual-conditioners. The mechanistic behaviour and effectiveness of these dual-conditioning aids in dewatering of sludge were investigated in this study.

In addition to the assessment of sludge dewaterability, understanding the consequential change of sludge rheology during the conditioning step is critical as it plays a fundamentally important role in analysing the hydrodynamic behaviour of sludge, as it flows through the treatment process. Rheological properties of sludge suspensions produced from various treatment processes will strongly influence working conditions and scaling-up calculations of tanks, settlers, pumping stations or installations for sludge transport and storage. In particular, the study of sludge rheology for conditioning and dewatering processes is markedly difficult as it involves flocculated and coagulated suspensions where the structure of the flocs is at non-equilibrium. The rheology depends not only on the magnitude of the attractive energies but also how the flocculated or coagulated structures are formed (Tadros 2010). Therefore a better understanding of the flow properties of sludge is required in order to obtain useful parameters to improve the design of sludge treatment processes and to ensure sustainable sludge management. For this study, it was hypothesised that sludge rheology may provide fundamental information on the characteristics of sludge for optimum conditioning, particularly for the determination of chemical dosages and improved dewatering process.

1.2 Scope and Objectives

With the aforementioned background, the present study aims to investigate the dewatering performance improvement of digested biological sludge. This was carried out by novel development of coagulating conditioning compounds in a municipal anaerobically digested (AD) sludge system. The study was extended to a chemically well-defined and representative synthetic sludge to gain a better understanding of the conditioning and dewatering characteristics due to the reproducibility of synthetic sludge for controlled experiments. Lastly, the selected conditioning aids were tested on a septic sludge system for comparison along with extended application to dual-conditioning method.

The specific objectives of this study are outlined as follows:

- Study on the characteristics of digested biological sludge as it has a very important effect on the dewatering performance
- Investigate the effect of various physicochemical process parameters of the conditioning chemicals that influence dewatering
- Study on the role of cationic polyelectrolytes and other inorganic compounds as conditioning aids in sludge dewatering
- Study the comparative effect of organic and inorganic conditioning aids on the dewatering performance
- Investigate the mechanisms of conditioning in enhancing water removal from sludge using different conditioning aids
- Determine the optimal conditioner dosages corresponding to various sludge dewaterability measurements
- Explore the rheology of conditioned sludge and its role on the dewatering performance
- Evaluate the application of single and dual-conditioning aids to improve sludge dewaterability

1.3 Significance

- The most significant environmentally sustainable outcome of this study is the development of a feasible strategy in the reduction of sludge volume and hence minimisation of sludge handling cost.
- Novel conditioning aids such as chitosan, copolymer and cations of different valences as well as dual-chemical conditioning are investigated in order to present a better understanding of their mechanisms and roles in sludge dewatering.
- Rheological parameters are very important in sludge management, not only as design parameters in transporting, storing, landfilling and spreading operations but also as control parameters in operations such as the stabilisation and dewatering processes.
- Dewatering of sludge is of significant economic and environmental importance to the minerals, chemicals and water treatment industries. In addition to the financial incentives, sludge dewatering provides environmental benefits as a result of enhanced water recovery, and in the case of mineral industry, safer tailing disposal.
- Sludge dewatering improves the quality of biosolids which have different beneficial applications such as soil conditioners and fertilisers in line with regulations and good agricultural practices.
- The needs in sludge dewatering and chemical conditioning are likely to expand in the future for the other types of organic slurries. In particular, an increase in the use of biomass, such as microalgae, for energy production will lead to the extensive use of dewatering operation for further processing or disposal of the residual solids.

1.4 Organisation of Thesis

This thesis has been organised into eight chapters to allow focused discussion on different areas. Chapter 1 addresses the motivation and background of this study. Research scope and objectives, as well as their significance in various aspects are included. Chapter 2 reviews the sludge processing background, understanding on conditioning and dewatering, relevant mechanisms and parameters, and some up-to-date information on advances in sludge conditioning and dewatering. Chapter 3 provides guidance for conducting the research methodology in order to address the research objectives presented in Chapter 1. Results and discussion are presented in Chapters 4, 5, 6 and 7, with emphasis on sludge characteristics, dewaterability, rheology and dual-conditioning, respectively. Wherever possible, Chapter 6 on sludge rheology provides comparative dewaterability performance from Chapter 5. A brief section on process optimisation using response surface method (RSM) design is included in Chapter 6. Lastly Chapter 8 summarises the overall work with recommendations for future directions. Detailed sample calculations and supplementary rheograms along with data are given in the Appendices. Figure 1.1 provides an overview of the organisation of the thesis.

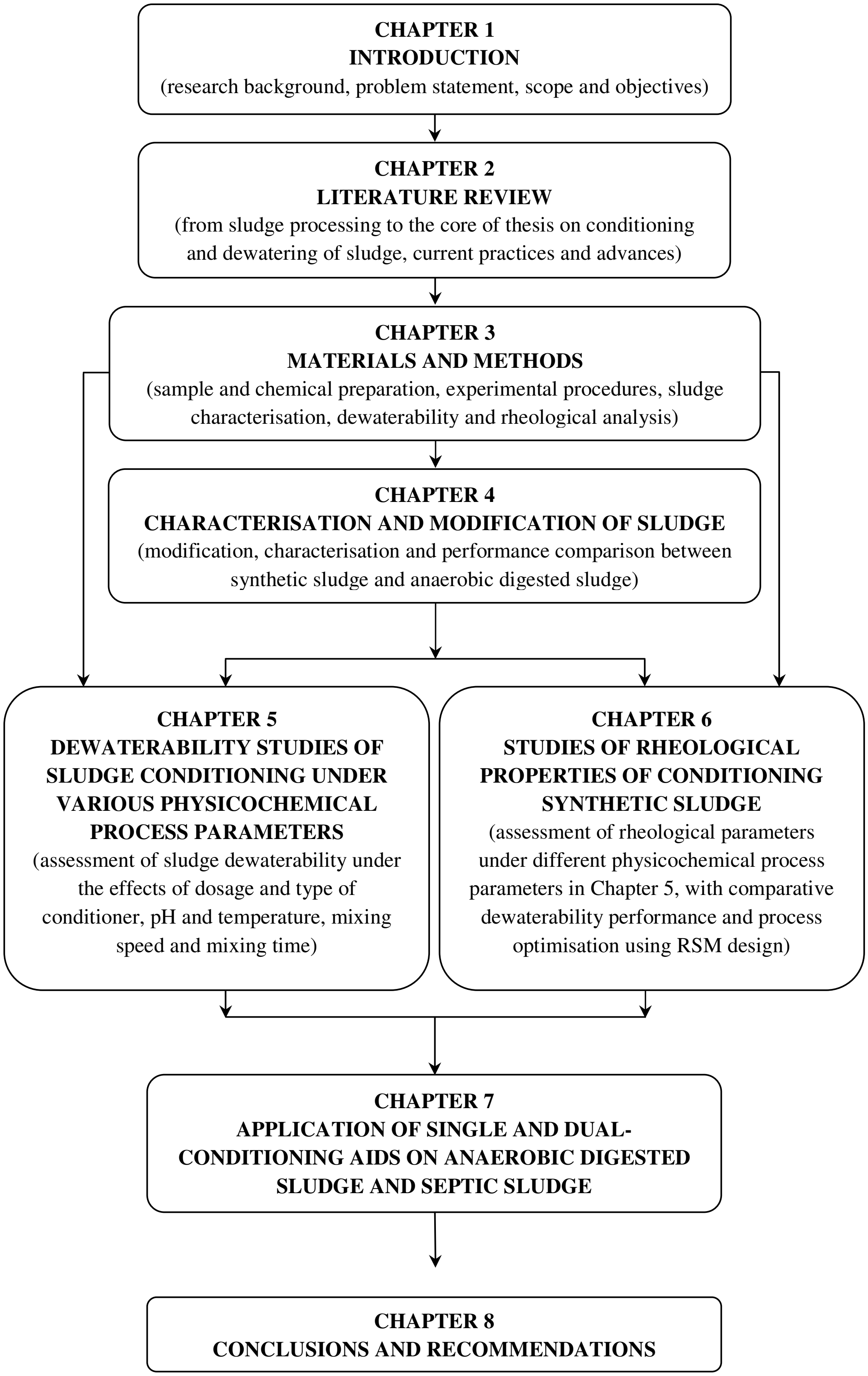

Figure 1.1 Organisation of thesis

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CHAPTER 2

LITERATURE REVIEW[*]

Sludge management accounts for a major part of the costs of the wastewater treatment processes and represents significant technical challenges. In many wastewater treatment facilities, sludge dewatering is identified as the bottleneck of the sludge handling system. The high sludge volume and high water content in addition to the colloidal and compressible nature of sludge cause handling and processing difficulties. The application of conditioning aids in sludge dewatering is thus crucial to alleviate these problems. This chapter first addresses the pressing issues on sustainable sludge processing especially in sludge dewatering operations. The overview of sludge processing and how conditioning and dewatering come into the sequence of sludge processing are then presented. Various conditioning and dewatering methods are reviewed. The influencing factors, dewaterability parameters and mechanisms of conditioning are also presented for better understanding of sludge behaviour and its corresponding effect on dewatering performance when different conditioning aids are applied. Knowledge of the consequential change of sludge rheology during the conditioning step is critical as it plays a fundamentally important role in analysing the hydrodynamic behaviour of sludge, as it flows through the treatment process. Therefore various aspects of sludge rheology such as the rheological models and the use of rheology as a tool for optimal dose of conditioning aids are discussed. Lastly, current practices and advances in sludge conditioning and dewatering are presented in order to enlighten readers of the future trends and development of conditioning aids in sludge treatment.

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2.1 Introduction

Water is the most useful and essential resource of life. The use of water inevitably produces wastewater. When wastewater is treated to return this resource to the environment, it produces wastewater sludge. Without prior treatment, such as stabilisation (reduction of pathogenic organisms and odour) and dewatering (reduction of volume), sludge is not amenable to beneficial use as biosolids (Vesilind and Spinosa 2001). The processing, reuse and disposal of sludge must be managed in a cost-effective way, taking into account prevailing local, state and federal regulations. In particular, successful application of conditioning aids to enhance sludge dewatering is vital, with the main purpose of reducing dewatered sludge volume and hence making it a cost-effective process. The ultimate utilisation or disposal of sludge will often give a rough indication as of which conditioning aids may be more suitable for sludge dewatering process.

2.2 Sludge Processing: An Overview

In wastewater treatment processing, water contaminants are transferred into sludge which is to be treated and disposed of properly. Sludge is the by-product of wastewater treatment. Wastewater sludge can be defined as "a suspension of organic and inorganic particles into a fluid" (Novarino et al. 2010). The difference between the terms "sludge" and "biosolids" is determined by the way they are managed. If wastewater sludge is used for beneficial reuse (e.g., as a soil amendment or fertiliser), it is commonly called biosolids (Spellman 2009). Sludge is generated in primary, secondary, and chemical treatment processes in a wastewater treatment plant (WWTP). Although the quantity of sludge produced is only approximately 1% of the quantity of treated wastewater, sludge management costs 40 to 50% of the total wastewater treatment costs due to long processing time and use of complex equipment (Turovskiy and Mathai 2006).

As shown in Figure 2.1, various forms of sludge are produced from different unit operations during wastewater and sludge processing. Sludge cannot be disposed on land without treatment due to the presence of health risk and release of odours. Stabilisation operations such as aerobic digestion and anaerobic digestion (AD) are thus introduced after sludge thickening to reduce pathogens, offensive odours and organic decay from sludge (Metcalf and Eddy 2003). On the other hand, sludge may comprise as much as 97% water content which significantly affects the cost of disposal related to the volume of sludge being processed (Spellman 2009). Among the sludge processing unit operations presented in Figure 2.1, thickening, conditioning, dewatering, and drying are mainly used to reduce the water content (Metcalf and Eddy 2003). In order to separate as much of the water from the solids as possible, conditioning process is required before dewatering operation to enhance the effectiveness of water separation by altering sludge properties physically or chemically. A typical WWTP may involve chemically enhanced primary treatment sludge and thickened waste activated sludge (from dissolved air flotation) which are fed to the AD process followed by polymer conditioning and centrifugal dewatering system.

2.3 Sources and Characteristics of Sludge

Sludge exists in various forms and quantities. The origin of the waste, the type of treatment plant and the method of plant operation often affect the amount and quality of sludge produced (Vesilind 1979). Wastewater sludge may be classified based on their characteristics and origins, namely (a) primary sludge, (b) physico-chemical sludge, (c) activated sludge/thickened activated sludge, (d) mixed sludge, (e) aerobic digested sludge and (f) anaerobic digested (AD) sludge. Due to the wide variety of sludge, the development of methods for sludge characterisation and analysis as well as designs of sludge handling and disposal operations is taking place all the time. Vesilind (1979) proposed that both basic parameters and operational parameters are essential to understand the complex nature of sludge characteristics as summarised in Table 2.1.

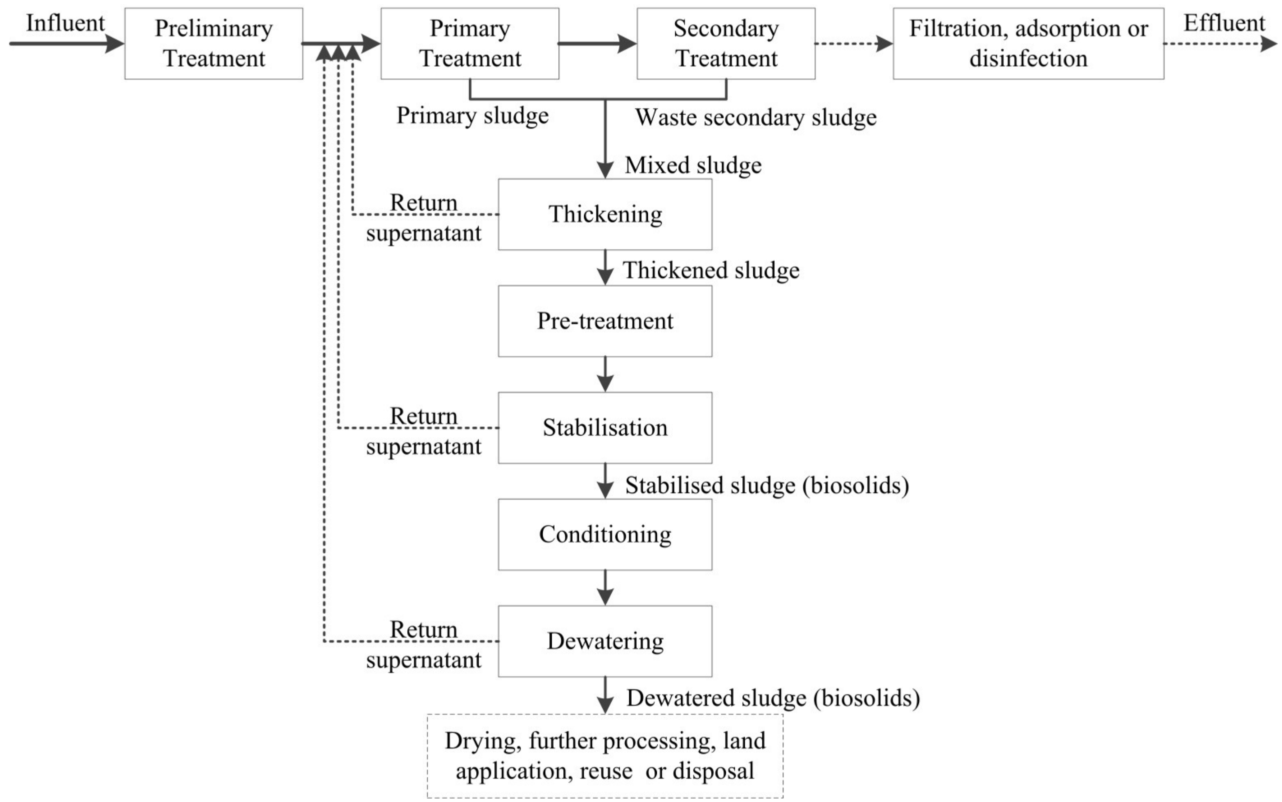


Figure 2.1 Wastewater and sludge processing flow diagram

Sludge characteristics can be broadly classified as (a) physical properties, (b) chemical properties, (c) biological properties, and (d) bio-chemical properties. Depending on the problem or method of disposal, only certain characteristics of interest will be helpful in the understanding of sludge behaviour. For sludge which is to be conditioned and dewatered in a dewatering operation, the characteristics of interest will be those of zeta potential, filterability and sludge cake solids content. Whereas, if the sludge is to be utilised as fertiliser, the nutrient concentrations will be the characteristics of interest (Vesilind 1979).

Table 2.1 Sludge characteristics

Physical properties	**Chemical properties**	**Biological properties**	**Biochemical properties**
Specific gravity	Heating value	Taxonomy (classification of organisms)	ATP (Adenosine triphosphate)
Solids concentration	Fertiliser value	Presence of pathogenic organisms	DNA (Deoxyribonucleic acid)
Settleability	Food value (animal feed)		Enzymes
Particle size and shape	Electrical charge (zeta potential)		
Distribution of water (by gravitational and centrifugal settling)	pH		
Rheology			
Others (odour, colour, filterability, drainability)			

2.4 Water Distribution in Sludge

The main component of sludge is water which is present in a number of different forms (Spellman 2009). Most past researchers have attempted to divide water in sludge into two categories, namely bulk water and bound water. Vesilind (1979, 1994) however suggested that various water fractions associated with the sludge floc can be defined on the basis of the sludge floc structure. In addition to bulk (or free) water, different forms of water could exist in sludge, including some fractions of interstitial water, vicinal water and water of hydration which sum to a total of bound water. Figure 2.2 presents the microscopic image of AD sludge corresponding to the various water fractions in a sludge floc as described by Vesilind (1994). It can be seen that water is captured in the interstitial spaces within flocs and within cells forming the fraction of interstitial water in AD sludge. Meanwhile vicinal water is illustrated as layers of water molecules held tightly to the particle surface by hydrogen bonding while water of hydration is chemically bound to the particles and removable only by the application of thermal energy. Vesilind (1994) further deduced that dewatering of polymer conditioned sludge can only remove the bulk and much of the interstitial water, but not the vicinal water.

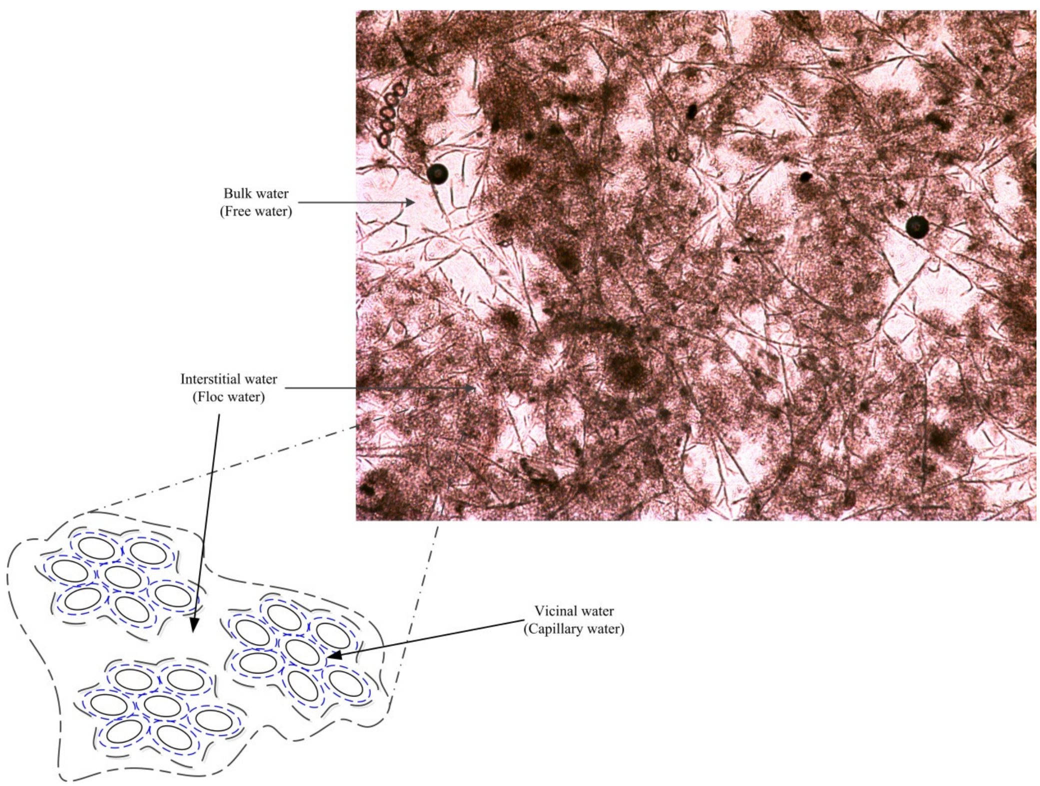


Figure 2.2 Presence of different forms of water in AD sludge

2.5 Anaerobic Digestion and Its Impact on Sludge Dewaterability

AD and sludge dewatering are the most widely used sludge treatment methods at WWTPs. Recently, AD has become one of the more commonly used stabilisation process in sludge management, providing effective pathogen destruction, reduction of volatile solids and odour potential, and an energy source in the form of biogas

(Ayol 2005). The potential of using biogas as energy source has long been recognised and current technologies are being developed to improve quality, to enhance energy use and to reduce the associated problems with the use of AD. Due to these advances, there are tendencies towards increased use of AD in many parts of the world such as Australia, China, India, Malaysia, the United States and Europe in past decades. It is estimated that the annual potential of biogas production in Europe is exceeding 200 billion m^3 with digestion of sewage treatment sludge as the major contributor (Appels et al. 2008). For these reasons, AD shows great potential to optimise the current WWTP, offering cost reduction and waste reuse.

AD is a biochemical degradation process that converts organic materials into simpler constituents in a series of metabolic interactions of a wide range of microorganisms that catalyses the process in absence of oxygen (Chong et al. 2012). AD is said to cause poorer dewatering characteristics in the residual sludge, causing higher chemical requirements in conditioning, lower quality of final processed sludge cake, and higher operation and disposal costs (Ayol 2005). Studies have shown that the release of protein and polysaccharide (biopolymer) into solution during AD results in an increase in the conditioning chemical demand and in the deterioration in dewatering properties, but this mechanism is unresolved (Novak et al. 2003, Novak 2010). Meanwhile Dentel (2001) claimed that the increase of ionic strength from the volatile acids present causes the conditioning polymers to become less extended due to the decreased repulsion between adjacent charged sites on the molecule. Although the use of some novel techniques such as ultrasound enhancement and thermophilic digestion is claimed to enhance the biogas production, increase solids reduction, improve dewatering and increase destruction of pathogenic organisms, a lot of uncertainties are present and more research is required to establish the feasibility of these techniques.

2.6 Conditioning and Dewatering of Sludge

Dewatering of sludge is of significant economic and environmental importance to the minerals, chemicals and water treatment industries. Disposal of sludge is costly and reduction of sludge volumes through improved dewatering can provide large cost savings. Therefore efficient wastewater sludge management frequently requires the use of dewatering processes so that the sludge cake can be transported by truck and applied as biosolids for beneficial agricultural applications, or disposed of by landfilling or incineration. In wastewater processing, dewatering refers to the removal of water from sludge to achieve volume reduction greater than that achieved by thickening which improves the subsequent handling of these solid-semisolid materials. Sludge dewatering can also improve airflow and texture before composting, reduce fuel demand for evaporation before thermal drying or incineration, and also reduce leachate production when sludge is disposed in landfill (Turovskiy and Mathai 2006).

It is well known that the solid particles in sludge are extremely fine and hydrated while carrying electrostatic charges which make dewatering rather difficult. Furthermore the higher the colloidal nature of sludge, the more difficult it is to dewater. Generally digested sludge possesses the highest colloidal characteristics compared to primary and secondary sludge. Besides, the permeability and compressibility characteristics of sludge render them unsuitable for direct introduction to dewatering equipment (Dick et al. 1980). It is necessary to improve sludge dewaterability to make mechanical dewatering processes viable. Sludge conditioning processes are used to alter the physical properties of sludge to make it amenable to dewatering. Wastewater sludge may be pre-treated or conditioned by a number of treatments to enhance water removal.

2.7 Conditioning Methods

Dick et al. (1980) defined the goal of conditioning as to increase porosity, particle diameter, particle shape factor, and particle mass density as well as to reduce the coefficient of compressibility, from the point of flow through porous media. Sludge conditioning methods involve chemical, physical or biological treatment to increase the efficiency of the downstream processes. Figure 2.3 shows the various conventional and novel conditioning methods according to their categories. Among all, chemical conditioning is the most common conditioning methods for sludge thickening and dewatering (Turovskiy and Mathai 2006).

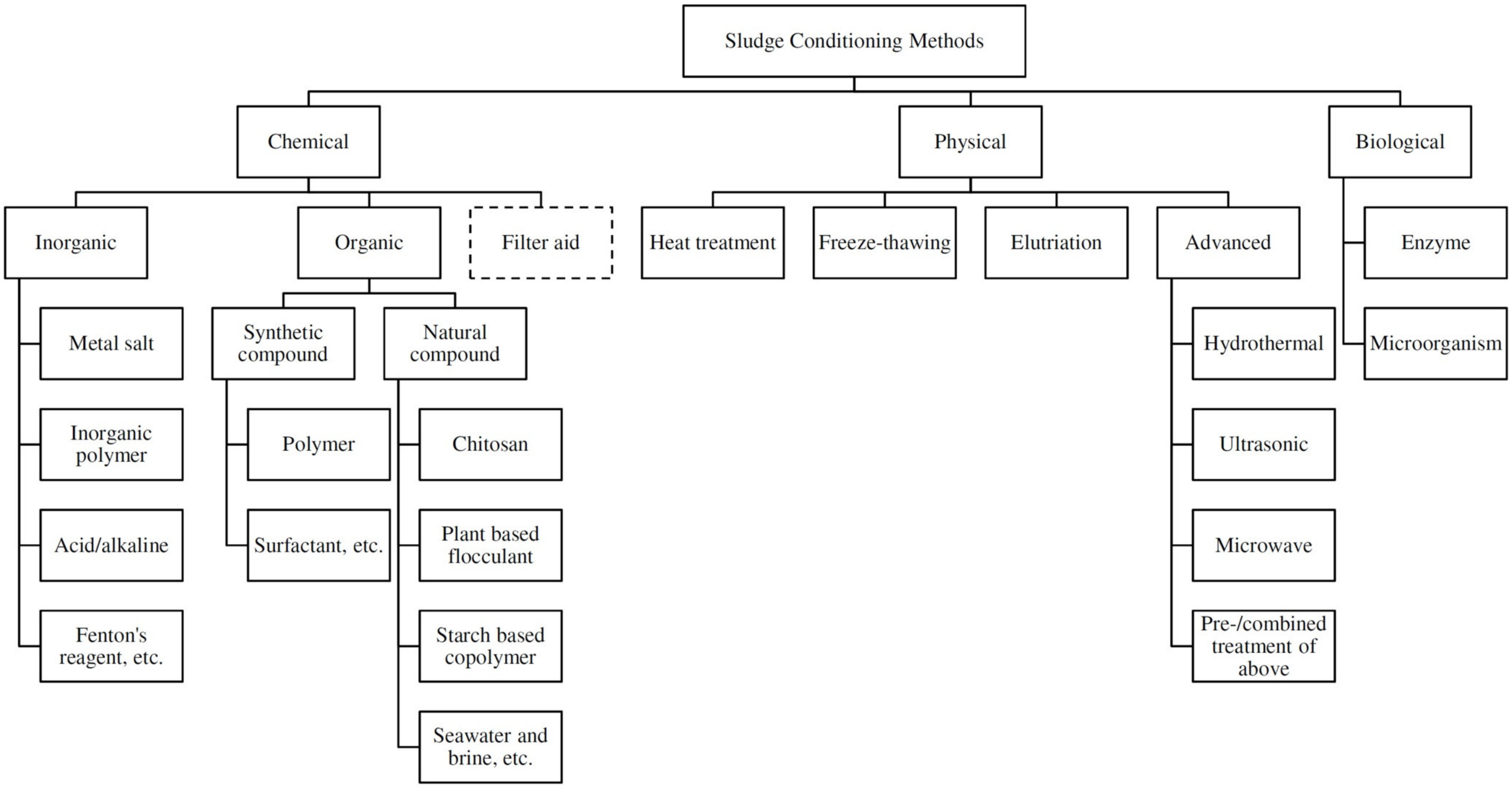


Figure 2.3 Classification of sludge conditioning methods

2.7.1 Chemical conditioning

Historically, chemical conditioning of sludge has been viewed as analogous to the coagulation/flocculation process used in water treatment (Dentel 2001). Thus the terms “coagulants”, “flocculants” and “conditioners” have been used interchangeably in literature for sludge conditioning. Sludge is known to be difficult to dewater, due to its high compressibility and its gel-like water retention capacity. To overcome this problem, chemical conditioning is performed with the main objective to increase particle size by combining small particles into larger aggregates via a two-step process of coagulation and flocculation. Coagulation destabilises the negatively charged particles by decreasing the magnitude of the repulsive electrostatic interactions between the particles. Flocculation then promotes the agglomeration of colloidal and finely divided suspended matter after coagulation by gentle mixing. In short, the addition of chemicals binds the fine sludge particles into larger flocs to enhance water removal from sludge (Zhang et al. 2014b). Both organic and inorganic chemicals can interact with sludge particles through coagulation and flocculation but the former have largely replaced the latter in most dewatering applications.

(a) Inorganic chemicals

Inorganic chemicals were the first conditioning agents applied to sewage sludge and have been prevalent throughout the 20th century. Many inorganic chemicals have been used in sludge conditioning, such as sulphuric acid, alum, chlorinated copperas, ferrous sulphate, ferric chloride with or without lime, and others (Cheremisinoff 2002). Among all, aluminium and iron salts are most extensively used due to their multivalent characteristic which effectively neutralises charged colloidal particles and produces rigid flocs within their structural networks. Their relative insolubility also aids their removal as hydroxide precipitates together with the sludge flocs. In recent years, a number of aluminium-based inorganic polymers such as polyaluminium chloride (PACl), polyaluminium sulphate (PAS), or polyaluminium chlorosulphate (PACS), are increasingly used worldwide as coagulants or flocculants for water and wastewater treatment, especially PACl (Tzoupanos and Zouboulis 2008). PACls are soluble in water and they react to form insoluble aluminium poly-hydroxides which precipitate together with sludge flocs.

(b) Organic chemicals

The use of organic polyelectrolytes, frequently called organic flocculants or polymers, in municipal WWTPs began during the 1960s (Water Environment Federation 2007). At the present time, wastewater sludge thickening and dewatering processes are heavily dependent on the use of organic polymers. In 2002, approximately US$188 million worth of cationic polyacrylamide (cPAM) flocculants were consumed for sludge conditioning in North America (Water Environment Federation 2007). With the prosperity and technological advances of polymer industry, polymer conditioning has become the most extensively used and operable practice among all the pre-treatment methods for improved dewatering process. Development of more sophisticated dewatering equipment, such as belt filter presses and centrifuges also contributes to the widespread use of polymers especially cPAM which represent almost 95 to 100 percent of the organic polymers used in sludge conditioning (Water Environment Federation 2007).

A number of advantages have been identified for the popularity of polymer conditioning. Additional sludge mass produced by polymer conditioning is less compared to the one using inorganic chemical conditioners such as lime and ferric chloride. Polymers do not lower the heating value if dewatered sludge is to be used as a fuel for incineration. They allow for cleaner material-handling operations and reduce operation and maintenance problems (Albertson 1991). Contrary to organic polymers, all of the inorganic coagulants are difficult to handle and their corrosive nature can cause maintenance problems in the storing, handling, and feeding systems in addition to the safety hazards inherent in their handling (Cheremisinoff 2002). Table 2.2 compares the various parameters as well as pros and cons in using inorganic and organic chemicals as sludge conditioners.

Table 2.2 Comparison between inorganic and organic chemicals as sludge conditioners

	Inorganic chemicals	Organic chemicals
Examples	Ferric chloride, ferrous sulphate, aluminium chloride, lime	Polymers or copolymers related to polyacrylamide (PAM)
Efficiency	High	High
Cost	Low	High
Dosage requirement	High	Low
Sludge cake produced	High	Low
Advantages	– Do not require aging time, thus no special mixing devices required – React with bicarbonate alkalinity to form hydroxides which give additional flocculating effect – Form permeable cake, good for low shear conditions – Struvite control – Advances in inorganic polymers reduce problems in using conventional inorganic chemicals	– Cleaner material-handling operations – Reduced operation and maintenance problems – Small storage space requirements – Less affected by pH – Good heating value – Advances in organic polymers (with natural compounds) provide convenient, environmental friendly, and high-performance products
Drawbacks	– Maintenance problems in the storing, handling, and feeding systems due to corrosive nature – Safety hazards inherent in handling	– Still high water content in the resulting sludge cake – Sticky sludge cake and filter media clogging may occur when dewatered with a filter press due to improper polymer selection and dosing – Concern over biodegradation and toxicity of acrylamide based polymers

(c) Filter aids as physical conditioners

Physical conditioners are inert compounds commonly used to enhance sludge dewaterability for sludge with high compressibility. They are often referred to as skeleton builders or filter aids for their role in building a rigid and permeable structure in sludge flocs. The addition of skeleton builders reduces the compressibility of sludge and improves the mechanical strength and permeability of the sludge solids during compression (Qi et al. 2011). Minerals and carbonaceous materials such as fly ash, cement kiln dust, gypsum, char, coal fines and cellulosic wastes have been used or evaluated as physical conditioners. These materials share some common characteristics that they are generally inert with relatively high porosity and rigidity.

Physical conditioners can be used alone or in combination with chemical conditioners to enhance sludge dewaterability. When used in combination with chemical conditioners, the interactions between the conditioners and sludge colloids occur due to the charged nature helping to bridge the sludge particles while forming a permeable solid structure at the same time which may lead to higher sludge dewaterability. With the current trend towards the high-productivity processes using low pressure and short contact time, such as using a belt press or centrifuge, the addition of a skeleton builder to improve sludge dewaterability may not be as significant. Qi et al. (2011) pointed out that only solid–liquid separation techniques operated at high pressure and long compression time, such as using a filter press, can be benefited most significantly by the use of a filter aid.

2.7.2 Physical conditioning

Physical conditioning is generally a simpler treatment process without the use of chemical additives prior to dewatering operation. Heat treatment, freeze-thawing and elutriation have been used to a limited extent in physical sludge conditioning (Metcalf and Eddy 2003). Sludge conditioning by heat treatment was developed in the U.K. in the 1930s, and has been used in the U.S. since 1970s (Dick et al. 1980). Interest in heat treatment has, however, declined significantly with decreasing new installations because of high capital cost (for corrosive-resistant, odour-control and high-pressure instrumentation), high maintenance and skilled operation required, highly polluted sidestream and odour production (Turovskiy and Mathai 2006, Metcalf and Eddy 2003). Freeze-thaw conditioning is another effective dewatering technology for difficult-to-dewater wastewater sludge (Metcalf and Eddy 2003). It is economically feasible for WWTPs in cold climates only where natural freezing enhances the dewatering characteristics of sludge by converting the sludge from gel-like residuals to granules that drain readily. Conditioning by elutriation involves washing of sludge with 2–6 times washwater (normally wastewater effluent) in order to remove certain soluble compounds which increase the conditioner requirement (Qasim 1999). A number of problems follows this treatment method such as the production of a dirty elutriate, buildup of fine solids, increased operation and subsequent separation costs (Vesilind 1979). As a result, this method is not used as extensively as it had been at present.

Despite concern on energy costs, novel methods applying high energy in the form of ultrasonic, microwave, electrical, thermal and mechanical treatments have continued gaining research interests in recent years either as pre-treatment or combined treatment to enhance digester performance and sludge dewaterability (Climent et al. 2007, Yeneneh et al. 2013). Sludge preheating at a lower temperature from redundant heat source may compensate the downsides of heat treatment in sludge conditioning (Metcalf and Eddy 2003). Various combined treatments such as freeze/thawing with electro-dewatering, hydrothermal with mechanical expression, and pressurised osmosis electro-dewatering are found effective to some extent to improve dewatering performance (Tuan and Sillanpää 2010, Citeau et al. 2012, Wang et al. 2014).

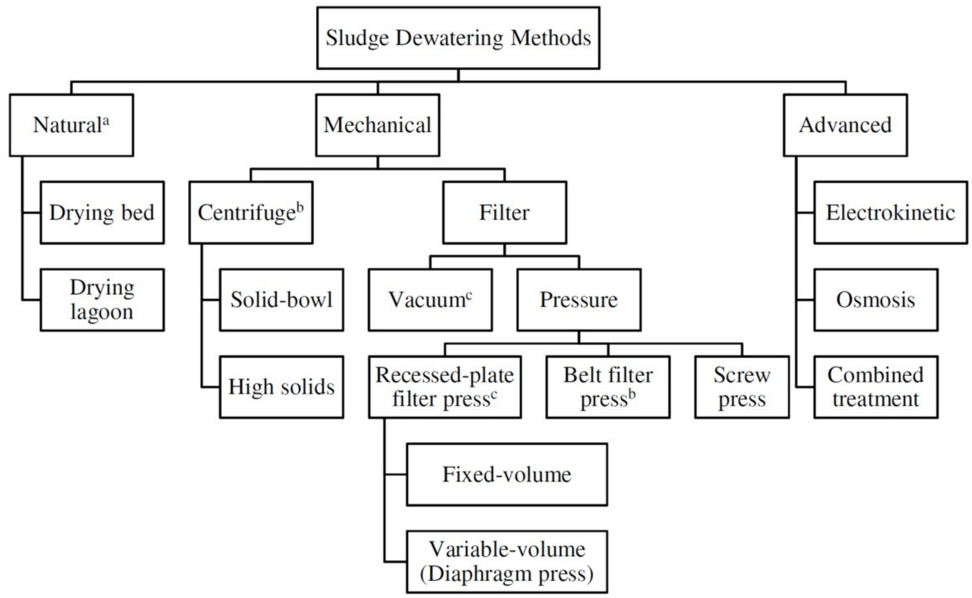
2.7.3 Biological conditioning

For sludge stabilisation process which involves microorganisms and microbial-environment conditions such as AD, the corresponding biological activities are crucial as their properties may impede sludge dewatering leading to additional polymer demand in chemical conditioning prior to dewatering processes. Enzymatic treatment has been reported effective in improving the dewaterability of AD sludge as the complex enzyme mixture of protease, lipase and other hydrolytic enzymes is believed to degrade the chemical constituents responsible for poor dewaterability (Ayol 2005). Parmar and his team (2001) investigated the treatment effect of enzyme mixture of fungal protease, yeast lipase VII, cellulase and biohemicellulase on AD sludge, and their results illustrated effective reduction of 50% of sludge solids and improved settleability properties of the treated sludge. Bioleaching is another emerging technology in recent years where it utilises a potential microbial method in the removal of sludge-borne heavy metals and enhancement of sludge dewaterability (Liu et al. 2012).

The application of microbial flocculants in sludge conditioning has attracted considerable research attention because of their biodegradability and good flocculating ability. To the best of our knowledge, only a limited number of strains such as *Bacillus* sp. (Liu et al. 2012), *Proteus* sp. (Zhang et al. 2010), and *Klebsiella* sp. (Liu et al. 2014) have been studied for enhancing the dewaterability of sludge. The use of a novel bioflocculant, TJ-F1, produced by *Proteus mirabilis* which was isolated from the activated sludge, has been found effective to promote dewaterability due to the presence of effective functional groups and bridging ability (Zhang et al. 2010). In another study by Liu and co-workers (2014), a novel bioflocculant named M-C11, produced by *Klebsiella* sp., was also isolated from the activated sludge and found to contain carboxyl, hydroxyl, methoxyl and amino groups with excellent stability over wide pH and thermal ranges which enhanced sludge dewatering.

2.8 Dewatering Methods

Dewatering is a physical solid-liquid separation unit after digestion process to produce drier sludge cake for easier handling and economical reuse or disposal. Dewatering processes are commonly classified into natural dewatering and mechanical dewatering as shown in Figure 2.4. Advancement in dewatering technologies introduces electrical field, osmosis, and combined treatment to further improve the dewatering performance. A few common dewatering methods for wastewater sludge are briefly described in the following sections.



[a] typically for unconditioned sludge
[b] typically for sludge conditioned with organic polymer
[c] typically for sludge conditioned with metal salt

Figure 2.4 Classification of sludge dewatering methods

2.8.1 Natural dewatering

Air-drying is a less complex dewatering method which removes moisture in stabilised sludge by natural expiration, evaporation, or induced drainage (percolation). It is easier to operate, and may be more energy-efficient than mechanical systems. Drying beds and lagoons are two such systems using air-drying principle. Drying beds have been used for years to dewater sludge based on gravity drainage followed by evaporation (Spellman 2009). Drying lagoons may be used as a substitute for drying beds especially for areas with high evaporation rates but the application is limited by increasingly stringent environmental regulations (Metcalf and Eddy 2003). Both systems often take up large land area and are vulnerable to weather change such as winter and rainfall (Water Environment Federation 2007). Besides, there are potentials for odour and vector problems as well as groundwater pollution (Metcalf and Eddy 2003).

2.8.2 Mechanical dewatering

Mechanical dewatering devices are common for facilities situated with limited land. Mechanical dewatering methods can be divided into two major types, which are the centrifugal dewatering and filtration dewatering (by vacuum or positive pressure). For sludge conditioned by organic polymers (usually polyelectrolytes), low-pressure dewatering processes such as centrifuge are often used as they work well with the large, loose sludge flocs formed. While inorganic chemical conditioning produces rigid flocs which often require high-pressure dewatering processes such as filter press (Zhang et al. 2014b). Until the mid-1970s, vacuum filters were the most useful mechanical dewatering systems. With the development of organic polyelectrolytes, vacuum filters have largely been replaced by belt filter presses and centrifuges in recent years (Water Environment Federation 2007).

For low-pressure application, solid-bowl centrifugal devices are often used for both sludge thickening and dewatering. Solids concentrations in the sludge cake may vary from 10–30% depending on the type of sludge while modified solid-bowl centrifuges with high torques (also called high-solids centrifuges) are capable to increase cake solids content to >30% (Metcalf and Eddy 2003). Addition of conditioning aids prior to the centrifugation process can further improve the solids capture. Plate and belt filter presses are two common types of high-pressure dewatering devices. A recessed-plate filter press induces dewatering by forcing the water from the sludge through the filter media under a high positive pressure (rather than vacuum) to achieve high solids capture and good filtrate clarity. A belt filter press, on the other hand, couples gravity drainage and mechanically applied pressure to dewater conditioned sludge. Both filter presses produce a good quality sludge cake at lower operation and maintenance costs than other mechanical dewatering systems but they require high construction and installation costs, skilled operators and chemical addition (Spellman 2009).

Electric field-assisted dewatering, also called electro-dewatering, has recently received increased research interests in the fields of fine-particle sludge, gelatinous sludge, sewage sludge, pharmaceutical industries, food waste and bull kelp (Mahmoud et al. 2010). This technology combines a conventional dewatering device with electrokinetic effects to enhance the dewatering rate and increase the final dry solids content with low energy consumption compared to thermal drying. Mahmoud et al. (2011) claimed that the use of an electric field combined with mechanical compression requires less than 10 and 25% of the theoretical thermal drying energy for the range of voltages between 10–50 V. Extended research suggested the combination of pressurised electro-osmotic dewatering technology to enhance dewatering efficiency, especially for the separation of bound water from sludge (Feng et al. 2014). Although the application of electrical field in sludge dewatering is at the trial stage, it is believed that with the development of new materials and technologies, and the more widespread application of combined separation techniques, electro-dewatering processes will play an increasingly larger role in separation processes.

2.9 Factors Influencing Sludge Conditioning and Dewatering

Sludge must be conditioned before it can proceed to dewatering process. The fundamental purpose of sludge conditioning is "to cause the aggregation of fine solids by coagulation with inorganic chemicals, flocculation with organic polymers, or both" (Cheremisinoff 2002). Several important factors such as sludge characteristics, sludge handling, and sludge coagulation and flocculation, may influence the conditioning process and hence the dewatering abilities of sludge.

2.9.1 Sludge characteristics

The complexity in sludge characteristics essentially affects sludge conditioning and dewatering. The organic matter content and the colloidal nature of sludge vary from various sources. As a general rule, biological sludge is more difficult to dewater and thus requires higher dosage of conditioner than those required by primary sludge. However the conditioning requirements may vary from plant to plant for the same source of sludge (Turovskiy and Mathai 2006). The age of sludge also affects the conditioning performance as the long stored sludge induces higher degree of hydration and more fines content which requires more conditioning chemicals than fresh sludge does.

In terms of sludge solids concentration, it is generally understood that the lower the solids concentration is, the lower the conditioner dosage requires. However a higher solids concentration has advantage of producing effective conditioning over a wide range of dosage when organic polymers are used where the process is less prone to overdosing (Turovskiy and Mathai 2006). Smaller particles and greater number of small particles cause adverse effect to conditioning performance. Both factors increase the surface area/volume ratio causing higher chemical demand and increased resistance to dewatering at the same solids concentration.

Meanwhile, the performance of inorganic conditioners is more sensitive to the change in pH and alkalinity than those using organic polymers. Both the dosage of inorganic chemicals and the alkalinity of the sludge itself affect the pH of the conditioning process. Another common known factor affecting sludge conditioning is the surface charge of sludge solids. The presence of a number of functional groups such as the hydroxyl and carbonyl groups in sludge solids causes it to be negatively charged and thus repel one another. The presence of difficult-to-remove bound water on the surface of sludge solids also affects the effectiveness of conditioning.

2.9.2 Sludge handling

Storage, pumping, dosing and mixing processes affect the following conditioning process to various extents. As mentioned in the previous section, a long period of sludge storage time affects the sludge content and thus requires more conditioning chemicals. The pumping process also causes some reduction in particle size from the resulting shear forces. When the sludge reaches the dewatering unit, proper mixing is required to evenly disperse the conditioning chemicals so that the chemicals may contact each sludge particle to capture those particles in a floc. The sequence of chemical addition, intensity of mixing, and duration of mixing are three mixing factors which may affect the sludge conditioning process. Short-duration, high-intensity mixing is required for dispersing the polymer solution effectively into the sludge while longer-duration, low shear mixing is required to flocculate the particles into larger agglomerates (Water Environment Federation 2007). Excessive shear or mixing should be avoided to prevent breakage of flocs of polymer–sludge particles.

2.9.3 Sludge coagulation and flocculation

Sludge conditioning is a two-stage activity where the first stage involves coagulation (often called charge neutralisation or stabilisation) which eliminates the negative electrostatic charge on the sludge particle, and the second stage involves flocculation (or bridging) which allows agglomeration of sludge particles (Water Environment Federation 2007). Consequently, addition of conditioning chemicals to coagulate and flocculate sludge significantly impinges on the dewaterability of sludge. A critical design parameter in sludge coagulation and flocculation during the conditioning process is dosage. The dosage affects the rate of water removal, the solids content of dewatered sludge cake and subsequently the solids disposal cost. Selection of the right dosage from pilot studies, bench tests, and on-line tests is critical for good dewatering performance (Cheremisinoff 2002).

2.10 Sludge Dewaterability Parameters

Different dewaterability measurements have been adopted in literature. In practical terms, Novak (2010) pointed out three items of concern in dewatering, which are the rate of liquid removal through a cake of deposited solids, the solids content of the dewatered material, and the amount and type of chemical added to enhance dewatering. Evaluating the effectiveness of a conditioning chemical on full-scale equipment can be a tedious and expensive process due to the large number of commercially available chemicals. Several quick and easy tests have been developed to screen chemicals in the lab for sludge dewaterability and thus narrow the number of chemicals to be tested in full-scale experiments.

2.10.1 Capillary suction time

The capillary suction time (CST) test has been documented in Standard Methods for the Examination of Water and Wastewater (APHA 2012), a comprehensive reference for water and wastewater analysis jointly published by the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF) since 1905. It is one of the most common parameters used to evaluate sludge conditioning aids and dosages in research. The CST apparatus automatically records the time taken for liquid from the sludge to travel a specified distance on a sheet of chromatography paper by monitoring the conductivity change occurring at two contact points as illustrated in Figure 2.5. This simple and quick method uses the capillary suction pressure generated from the paper to draw liquid from the sludge. The elapsed time is indicative of the rate of water release from sludge which may be used to characterise the sludge dewatering performance.

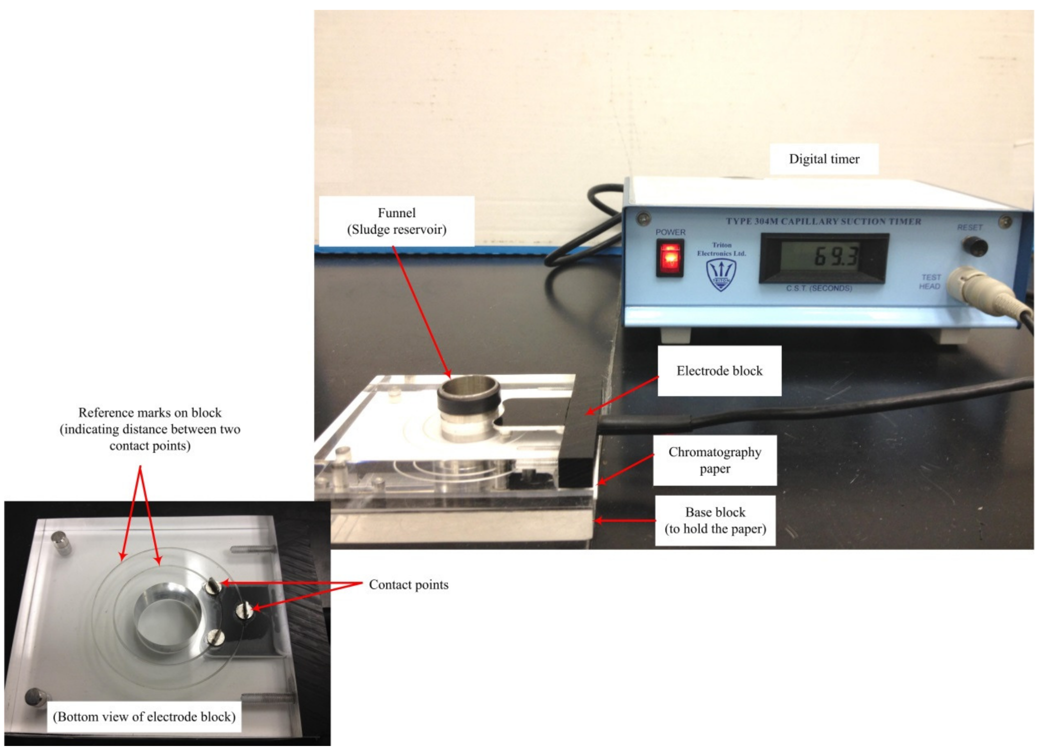


Figure 2.5 Capillary suction time apparatus

2.10.2 Specific resistance to filtration and time to filter

Specific resistance to filtration (SRF) can be calculated by performing laboratory filtration tests. The most common procedure employs a Buchner funnel where the funnel is connected to a vacuum source and a calibrated fluid reservoir (such as a graduated cylinder), and the volume of filtrate produced is recorded as a function of time and vacuum level (Dick et al. 1980). A simple filtration device using the Buchner funnel is illustrated in Figure 2.6. The measurement of this test is based on Darcy's law, where the resistance to the flow of water is caused by the surface friction of the particles assuming the sludge cake is a bed of small particles (Kopp and Dichtl 2001). The time to filter (TTF) test is another filtration test using the similar Buchner funnel apparatus like the SRF test and is documented in Standard Methods. It measures the time required for 50% of the original sample volume to collect in a graduated cylinder. The TTF test is superior to the SRF test due to its simplicity and ease of use (APHA 2012).

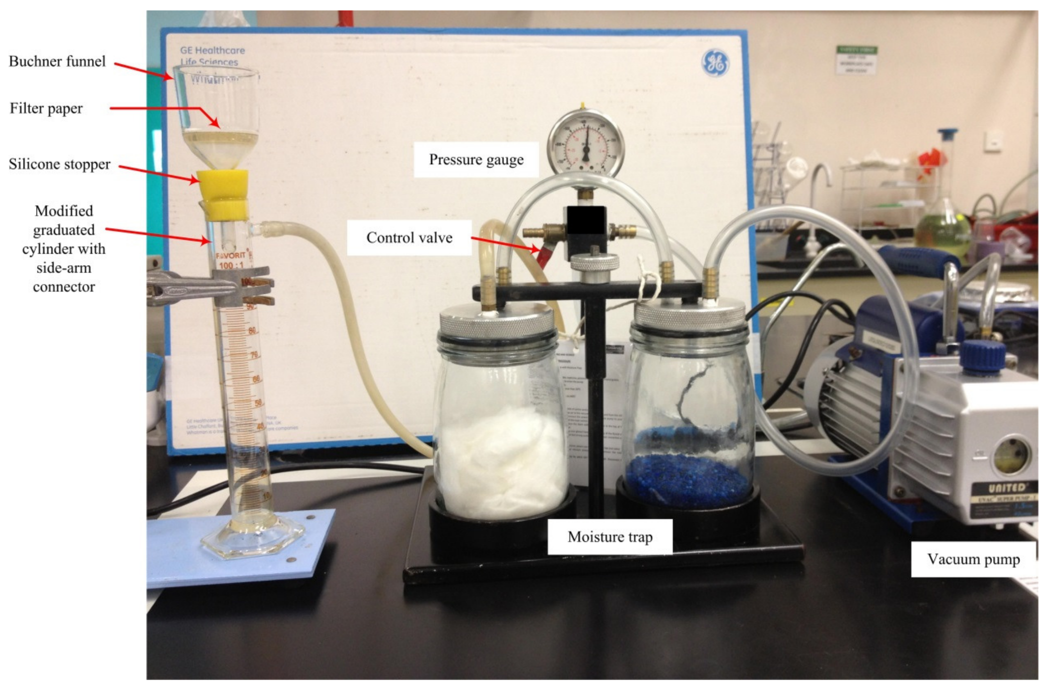


Figure 2.6 A modified filtration system for SRF test at Curtin University, Sarawak Malaysia

2.10.3 Cake solids content

In full scale plants where dewatering of sludge is typically carried out using belt filter presses or centrifuges, sludge dewaterability is expressed in terms of cake solids content or dry solids or water content in the dewatered sludge cake (Peng et al. 2011). The extent of dewatering is thus measured by the dewatered cake solids as the percent of dry solids. Peng et al. (2011) claimed that the normalised CST (i.e. CST divided by the initial total suspended solids) together with the measurement of dewatering extent (such as the bound water or dry solids content in sludge cake) should allow a perfect evaluation on the dewaterability of the activated sludge.

2.10.4 Zeta potential

Zeta potential (ZP) has been used to evaluate optimum polymer dosage when the ZP value in the centrate or supernatant after dewatering is close to ±0 mV (Kopp and Dichtl 2001). Dentel (2010) reviewed the colloidal stability by looking at the minimum CST which corresponds to the measurements of electrical charge in terms of streaming current and ZP in determining the optimum polymer dosage. Charge neutralisation was observed for cationic polymer where both streaming current and ZP values were close to zero. However, some researchers found that effective sludge conditioning does not require that particle charge and mobility be neutralised (Cole and Singer 1985, Kaseamchochoung et al. 2006). Krishnamurthy and Viraraghavan (2005) explained that prediction of optimum dosage cannot always be made by ZP measurements alone since not all dosing to achieve charge neutralisation led to effective sludge conditioning and there are no standard sample preparation procedures for sludge ZP measurement. However, ZP measurements provide a good basis for understanding the contribution of charge neutralisation to the conditioning process when used in conjunction with other dewaterability parameters.

2.10.5 Other parameters

Turbidity, geometric and rheological parameters have been used in a number of recent literature in studying sludge dewatering performance (Wang and Dentel 2011, Zhang et al. 2014b, Luo et al. 2015). In particular, floc size, porosity and network structural strength of the flocs have been used to indicate the resistance of flocs to shearing during mechanical dewatering operations. Advanced methods such as three dimensional excitation emission matrix (3D-EEM) spectra analysis coupled to fluorescence region integration (FRI) are alternative ways to evaluate the effect of conditioning (Zhang et al. 2014b). Relationships between various dewaterability parameters may be further studied to determine an all-embracing yet practical measurement combination for process optimisation.

2.11 Mechanisms of Chemical Conditioning

Decades ago, Dick et al. (1980) commented that "Sludge conditioning developed entirely as an art. The basic mechanisms by which conditioning processes transform the amorphous gel like sludge mass into a porous material which will allow release of water are not, in general, known". Thirty years later, available models of conditioning and dewatering are still insufficient to describe or optimise conditioning processes (Dentel 2010). With simplification, today's sludge conditioning process is generally described as a two-stage activity. The first stage is well known as charge neutralisation which occurs in a short time and eliminates the negative electrostatic charges on the sludge particles while the second stage, bridging, generally occurs in which individual sludge particles are held together by coiled strands of polymer or multivalent cation to form sludge flocs under slow and low shearing. Other mechanisms have been proposed as well but less discussed in sludge conditioning studies. Figure 2.7 summarises a few proposed conditioning mechanisms that enhance sludge dewatering. Depending on the conditions, often there is more than one mechanism occurring simultaneously or sequentially to make sludge dewatering possible.

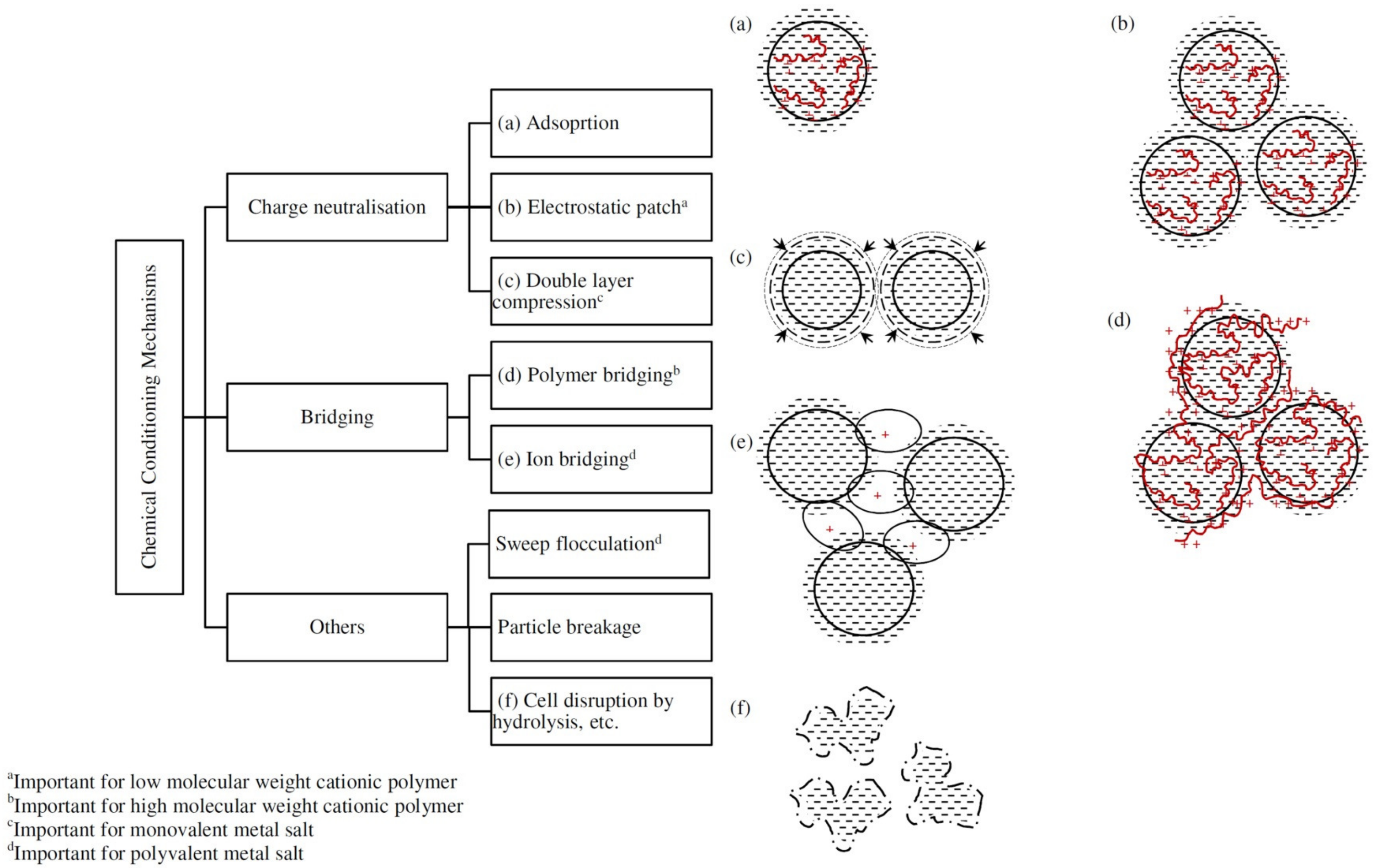


Figure 2.7 Sludge conditioning mechanisms

2.11.1 Charge neutralisation

The presence of surface charges due to the biological nature and the presence of weakly charged extracellular polymeric substances (EPS) are often said to contribute to the deterioration of sludge dewaterability (Mikkelsen and Keiding 2002, Curvers et al. 2009). Therefore the concept of charge neutralisation (also known as destabilisation or coagulation) has long been considered as an important aspect in chemical conditioning of sludge. The sludge is often visualised as a suspension of rigid, spherical particles stabilised by repulsive electrical interactions of their negatively charged surfaces (Dentel 2001, Dentel 2010). To overcome these electrical repulsions, adsorptive, cationic conditioning chemicals (usually polymers) are introduced into the sludge system where the electrostatic interactions give strong adsorption in the sludge-polymer system and that neutralisation of the particle surfaces can occur (Figure 2.7(a)). In addition, Dentel (2001) pictured the flocculation mechanism as a ‘patch’ model where the localised patches of opposite charge on opposing particles can eliminate the repulsion yet foster attraction between matching patches as illustrated in Figure 2.7(b).

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is often used in literature to predict this type of charge neutralisation. According to this theory, an energy barrier exists between two like-charged particles because of the interaction between a repulsive electrostatic component and an attractive van der Waals component from the particles (Dentel 2010). Reducing the outer potential of the particles with an oppositely charged ionic species (such as cationic polymer in coagulation conditioning) reduces the interparticle potential energy leading to a destabilised system. The energy barrier can also be eliminated by double layer compression through an increase in solution ionic strength such as adding cations or adjusting salinity and alkalinity (Figure 2.7(c)). Compression allows approach of the colloidal particles to where the attractive forces predominate over electrostatic repulsive forces and hence effects flocculation.

2.11.2 Bridging

According to Bolto and Gregory (2007), high molecular weight or long-chain polymers adsorbed on particles with loops and tails which can be extended into the solution and attached to other particles, thus ‘bridging’ particles together. Polymer bridging by long-chain polymers can give much stronger flocs than those formed by short-chain polymer or by metal salts as they have longer and extended cationic sites to bind to more than one particle (Figure 2.7(d)). Large flocs can be formed by long-chain polymers even under high shear conditions from common observation (Bolto and Gregory 2007). For inorganic conditioners such as lime with calcium ions, the divalent cations are said to act as a bridge between negatively charged sites on sludge due to their specific affinity and binding ability for the extracellular polymers, and thus an ion-bridging mechanism is proposed (Figure 2.7(e)) (Sanin et al. 2011). The ion-bridging effect may also explain the conditioning effectiveness of trivalent metal salts such as ferric chloride and alum with even stronger floc network formed as a result of extra cationic sites available.

2.11.3 Other mechanisms

The hypothesised combination of charge neutralisation and bridging is a simplification as it cannot explain some significant phenomena observable in the conditioning processes such as particle breakage due to the envisioned deformable, flexible and fragile assemblies and partial hydrolysis of the gel-like structure within the biological sludge (Dentel 2001, Dentel 2010). Therefore these investigators proposed that sludge should be viewed as a shear-susceptible matrix of polymeric filamentous constituents rather than as rigid spheres.

On the other hand, conditioning with inorganic salts (such as hydrolysed alum) is commonly associated to sweep flocculation mechanism where the colloidal sludge particles become enmeshed by the hydroxide precipitates formed at high pH as they aggregate. Sweep flocculation may occur under conditions where organic polymeric flocculants can be made to precipitate though this mechanism is less mentioned in most sludge conditioning studies. Solubilisation and removal of exocellular polymer as well as cell disruption due to hydrolysis have been proposed to account for the action of new conditioning aids such as surfactant and enzyme (Figure 2.7(f)) (Ayol 2005, Chen et al. 2001, Erdincler and Vesilind 2000a). Understanding of conditioning mechanisms is expected to expand continuously with development of sophisticated measuring devices and discovery of novel conditioning aids.

2.12 Sludge Rheology

The safe, efficient and economical transfer of sewage sludge in WWTPs and in sludge treatment facilities is of great importance. For that reason, mechanical and rheological characteristics of sludge must be determined. Chemical additives like polymers or mechanical operations affect sludge properties like rheological properties. Sludge rheology will provide the fundamental information on the characteristics of sludge for optimum chemical conditioning. The sludge viscosity could also be used as a control parameter to optimise the dosage in chemical conditioning.

2.12.1 Sludge rheological models

Most sludge suspensions do not obey Newton's law of viscosity. The flow behaviour can be evaluated from plots of shear stress versus shear rate (also known as flow curves or rheograms) as shown in Table 2.3. The following sections discuss the most commonly used equations to represent the non-Newtonian behaviour of sludge, namely the Bingham, the Ostwald or power-law, the Herschel–Buckley, the Sisko, and the Casson equations (Seyssiecq et al. 2003).

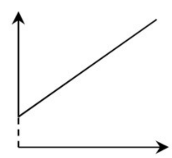
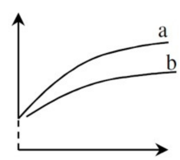
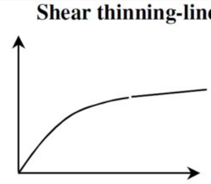
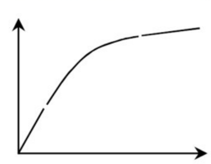
(a) Bingham model

The Bingham model has been used to fit the rheological behaviour of AD sludge at high shear rates (about 550–1500 s^{-1}) (Baudez et al. 2011). The Bingham sludge system exhibits a shear stress/shear rate behaviour with a constant viscosity for stresses above the yield value and can be fitted to a linear equation as follows (Baudez et al. 2011, Eshtiaghi et al. 2013):

$$\tau = \tau_0 + \eta\dot{\gamma} \tag{2.1}$$

where τ is the shear stress in Pa and $\dot{\gamma}$ the shear rate in s^{-1}. The system shows a yield stress value τ_0 that can be obtained by extrapolation to zero shear rate. The slope of the linear curve gives the plastic viscosity (η), often termed as Bingham viscosity (η_B). Tadros (2010) noted that the value of τ_0 obtained depends on the shear rate range used for the extrapolation procedure.

Table 2.3 Features of some common sludge rheological models

Shape of flow curve (shear stress against shear rate)	**Without a yield stress**	**With a yield stress**
Linear 	**Newtonian** - Dilute sewage sludge	**Bingham** - Plastic behaviour - Intermediate to high shear range
Shear thinning 	**Power-law** - Pseudoplastic behaviour - Low to intermediate shear range	**Herschel-Bulkley[a]** - Yield pseudoplastic behaviour - Low to intermediate shear range - Concentrated sludge **Casson[b]** - similar to Hershel-Bulkley with a more gradual transformation over the discontinuity
Shear thinning-linear 	**Sisko** - Combined shear thinning and Newtonian at high shear range	
Linear-shear thinning-linear 	**Cross** - Combined shear thinning and Newtonian at low and high shear ranges	

(b) Power-law model

The power-law model has been used to fit the shear thinning behaviour of various sludge such as mixed primary and secondary sludge, polymer treated sludge, aerobic digested sludge and AD sludge typically at lower shear rates (0–100 s^{-1}) (Novarino et al. 2010, Ayol et al. 2006, Wang and Dentel 2011). The power-law sludge does not show a significant yield stress value and the apparent viscosity decreases with an increase in the shear rate for shear thinning behaviour. The flow curve can be fitted to the following power-law model, also known as the Ostwald-de Waele model (Peker and Helvaci 2008):

$$\tau = K\dot{\gamma}^{m} \tag{2.2}$$

where K is the consistency index and m is the shear thinning or flow behaviour index (also called viscosity or power index) where $m < 1$. K is the value of the shear stress when $\dot{\gamma} = 1$. The model becomes identical to Newton's model when $m = 1$, or to a shear thickening or dilatant fluid when $m > 1$.

(c) Herschel-Bulkley model

The Herschel-Bulkley model has been found common in a number of sludge rheological studies because it takes into account the yield pseudoplasticity of sludge (Baudez et al. 2011, Markis et al. 2014, Slatter 1997). This model fits most flow curves with a good correlation coefficient, and hence is the most widely used model for measurements under steady state. The Herschel-Bulkley model exhibits shear-thinning behaviour obeying the power-law at stresses greater than the yield stress (Peker and Helvaci 2008, Markis et al. 2014).

$$\tau = \tau_0 + K\dot{\gamma}^{m} \tag{2.3}$$

(d) Casson model

The Casson model is similar to the Herschel-Bulkley model but with a more gradual transformation over the discontinuity in the rheological behaviour (Peker and

Helvaci 2008). This model has been applied in a recent study of activated sludge rheology which showed comparable results to the Herschel-Bulkley model in prediction of viscosity (Khalili Garakani et al. 2011). It is commonly included in sludge rheology review (Seyssiecq et al. 2003, Eshtiaghi et al. 2013).

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta_C \dot{\gamma}} \qquad (2.4)$$

A plot of $\sqrt{\tau}$ versus $\sqrt{\dot{\gamma}}$ should give a straight line where τ_0 and η_C can be calculated from the intercept and slope of the line. Straight lines from the Casson model are only obtained from the results above a certain shear rate, thus care should be exercised when using the equation (Tadros 2010).

(e) Sisko model

Some shear thinning systems show a limiting viscosity in the low shear rate regime, and another limiting viscosity in the high shear rate regime. These two regimes are then separated by a shear thinning behaviour (Tadros 2010). For sludge system, the Sisko equation is more often encountered and is used to correct the limiting viscosity at high shear rate (η_∞) with a value of $m < 1$ (Seyssiecq et al. 2003, Peker and Helvaci 2008).

$$\tau = \eta_\infty \dot{\gamma} + K \dot{\gamma}^m \qquad (2.5)$$

2.12.2 Factors affecting rheological parameters

Rheological parameters such as the sludge viscosity are affected by different factors including the solids concentration, the surface charge, the solution pH, the EPS content, the size of sludge particles and the temperature (Pevere et al. 2009). The particle-particle interactions and the qualitative features of the sludge suspension are fundamental to the understanding of factors affecting the rheological parameters as summarised in Figure 2.8.

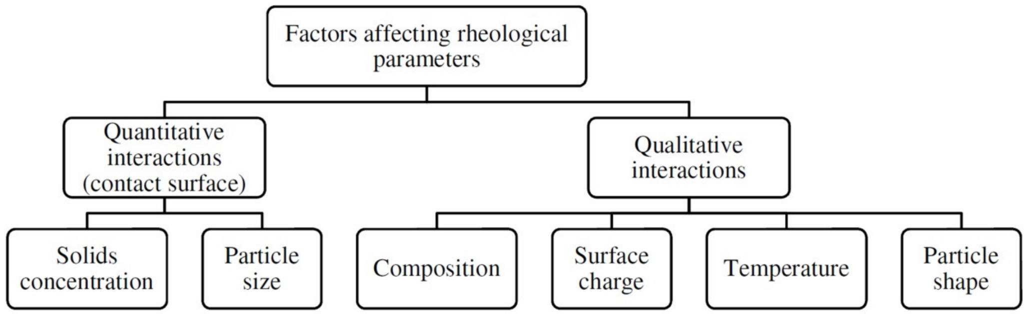


Figure 2.8 Quantitative and qualitative interactions that affect sludge rheological properties

(a) Effect of solution pH and surface charge

As discussed earlier, the solution pH is known to affect the surface charge of sludge due to its biological nature. A study conducted by Pevere et al. (2009) revealed that the pH affects the evolution of the viscosity of the sludge but the extent of the increase in limit viscosity mainly depends on the origin of the sludge. The presence of increased negatively charged surfaces due to different sludge composition will also increase the sludge viscosity.

(b) Effect of solids concentration

Several authors reported an increase in rheological parameters such as the viscosity and yield stress with increasing sludge solids concentration (Markis et al. 2014, Baudez et al. 2011). They explained the resulting rheological behaviour as a consequence of the increased particle interactions due to increased concentration causing the formation of more links between the flocs and thus a stronger network structure. Baudez and Coussot (2001) classified this network of interactions within the sludge as hydrodynamic interactions (between solid particles and surrounding fluid) and non-hydrodynamic interactions (between solid particles). The former can be represented by the Bingham whilst the later by the yield stress.

(c) Effect of temperature

Increase in temperature will generally result in a decrease in sludge viscosity. According to Eshtiaghi et al. (2013), an Arrhenius type equation can be used to describe the relationship of sludge viscosity and temperature as follows:

$$\eta_L = K \exp\left(\frac{E_a}{RT}\right) \tag{2.6}$$

where η_L is limit viscosity, K the empirical constant, T the absolute temperature, R the universal gas constant, and E_a the activation energy. Pevere et al. (2009) however reported that the viscosity is not significantly affected by the temperature range investigated (20–60°C), meaning that the mesophilic (35–37°C) and thermophilic (45–60°C) AD may only be marginally affected by the temperature difference. On the other hand, Baudez et al. (2013) found that both the impact of temperature and thermal history are important parameters that affect the sludge rheological characteristics. Sludge becomes less viscous as the temperature increases in the range of 10–60°C. Thermal history of preheating is said to release the dissolved constituents from sludge solids which then increases the viscosity and reduces the yield stress.

(d) Effect of particle size and shape

Similar to the effect of solids concentration on viscosity of sludge, reducing the particle size attributes to an increase of inter-particle interactions and hence an increase in viscosity. According to the work of Pevere et al. (2006), the limit viscosity value increases with decreasing size which increases the surface area of particle to interact with each other. In another work conducted by Pevere et al. (2009), the shape of sludge particle was found to affect the rheological parameters as well. The sludge with a rough surface presents a viscosity higher than the sludge with a smooth surface for the same solids content and comparable surface charge. The researchers believed that the roughness of the surface induces a resistance to the flow, and thus induces a stronger viscosity under the effect of shear.

2.12.3 Rheology as a tool for optimum control of conditioning aids

In sludge conditioning process, the sludge rheogram based on its non-Newtonian fluid property has been identified as an important tool for polymer dose control since 1980s (Wang and Dentel 2011, Campbell and Crescuolo 1982). Rheological parameters such as viscosity and yield stress can be obtained from sludge rheograms for the optimisation of sludge conditioning and dewatering operations (Wang and Dentel 2011, Ruiz-Hernando et al. 2013).

(a) Viscosity

Viscosity is a basic physical property used to describe the deformation and flow properties of sludge suspension. The term "apparent viscosity" has been used to describe the non-Newtonian fluid behaviour of changing viscosity with shear rate or applied stress (Eshtiaghi et al. 2013). Campbell and Crescuolo (1982) defined the apparent viscosity at any shear rate as "the slope of a line drawn from that point on the curve to the origin". A typical plot of apparent viscosity against shear rate for a shear thinning fluid is presented in Figure 2.9. It can be observed that with increasing shear rate, the apparent viscosity reduces from zero shear viscosity to infinite shear viscosity for the shear thinning fluid. The apparent viscosity has been used frequently in the literature to study sludge rheological features (Pevere et al. 2006, Markis et al. 2014).

Pevere et al. (2009) proposed to use the rheological parameter, "limit viscosity" (obtained from a plot of apparent viscosity against shear time in steady shear flow as shown in Figure 2.9) as a universal parameter to obtain information about the physico-chemical characteristics of sludge. On the other hand, Dentel and Abu-Orf (1995) suggested that the liquid stream viscosity (i.e., the centrate viscosity) has the potential to be used as a control parameter to continuously optimise the polymer feed rate for full-scale dewatering processes. Campbell and Crescuolo (1982) reported a parameter called the "instantaneous viscosity", which is the derivative of the flow curve, to be used as a control parameter for optimal conditioning.

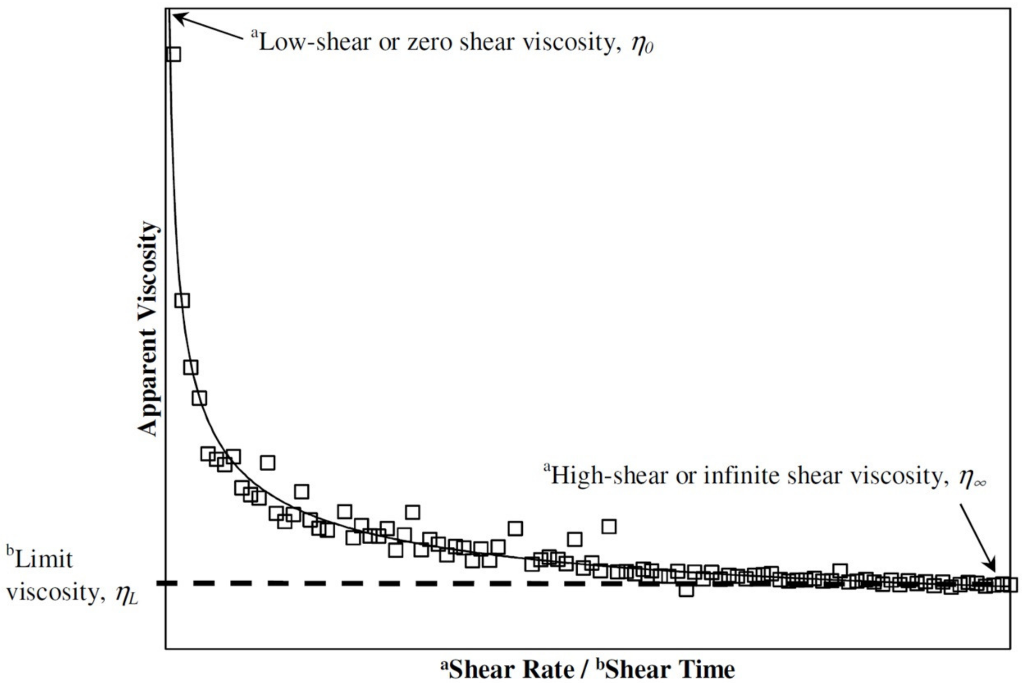


Figure 2.9 Various viscosity terms as rheological parameters for a shear thinning fluid

(b) Yield stress

Seyssiecq et al. (2003) pointed out that a quantitative knowledge of the yield stress is vital to determine the optimum operation conditions in WWTPs. The existence of the yield stress can be linked to the formation of a fractal interconnected network as previously described for aggregated sludge flocs as gel-like structures. Therefore it serves as a good indicator to characterise conditioned sludge flocs with respect to the network strength and structure, and hence in determining the optimum conditioning. Yield stress value can be determined experimentally in flow measurement in which a rheogram is obtained to calculate the yield stress by extrapolation of flow curve to zero shear using rheological models of sludge (Eshtiaghi et al. 2013).

(c) Rheogram peak

Some early researchers raised the ambiguity in defining and calculating the viscosity and yield stress value for the non-Newtonian systems (Campbell and Crescuolo 1982). Using a rotational viscometer in the rheological measurements, they suggested that the initial peak appeared in the rheogram would correspond to a zero derivative which could be used as a process control parameter for optimal sludge conditioning. With advancement in the measuring devices, similar hypothesis was proposed by several researchers who utilised the peak values from the rheograms to optimise the sludge conditioning performance (Ayol et al. 2006, Wang and Dentel 2011).

(d) Thixotropy

Most sludge is thixotropic where their internal structures break down as a function of time and shear rate. The degree of thixotropy is measured by the displacement of the increasing and decreasing curves of shear cycles which is known as a hysteresis loop (Campbell and Crescuolo 1982). Thixotropy has been used by Ruiz-Hernando et al. (2013) together with other rheological parameters such as viscosity and yield stress to assess the conditioning methods for optimum dewaterability.

2.13 Current Practices and Advances in Sludge Conditioning and Dewatering

Current practices in sludge dewatering operations still rely heavily on chemical conditioning prior to mechanical dewatering. The use of acrylamide-based polymers is favoured over the use of ferric chloride and alum as the latter drastically reduces the organic matter or thermal value of the dry sludge cake, which is unfavourable for subsequent disposal or reutilisation, despite its handling and operational drawbacks. It is evident nowadays that the research tendency in chemical conditioning is gearing towards three directions, i.e., the replacement or supplement of the commonly used acrylamide-based polymers by natural or biological compounds, the production of modified composite chemicals which are more complicated but more effective when compared with the traditionally applied chemicals, and the compound use of organic chemicals, inorganic chemicals and/or skeleton builders (also known as dual-conditioning). Table 2.4 summarises the evolution of several chemical conditioning aids over the past fifteen years.

For example, the emerging usage of plant-based coagulants such as nirmali seeds (*Strychnos potatorum*), *Moringa oleifera*, tannin and cactus for water, wastewater and sludge treatment has been identified by several researchers (Yin 2010, Betatache et al. 2014). Though some of these applications are limited to treatment of water or dilute effluent, these novel materials are technically promising to be used in sludge dewatering via coagulation and flocculation. Treatment of sludge with enzyme or microbial flocculants to enhance sludge dewaterability has been reported to be effective but these methods often require meticulous preparation or long treatment time (Liu et al. 2012, Ayol 2005, Zhang et al. 2010). Seawater and brine conditioning are found to improve the dewaterability of activated sludge in a more economical way due to their low prices and wide sources (Liu et al. 2011). However there is a concern of more liquor effluent produced or returned to the plant after mechanical dewatering since the volume of seawater or brine added could go up as high as the amount of sludge to be treated. The application of chitosan in water and wastewater treatment is well recognised but more studies are required when it comes to sludge dewatering application where specific measurements with respect to sludge dewaterability and rheological properties have not been explored in details (Kaseamchochoung et al. 2006).

For modified composite chemicals, recent research has focused in understanding the various characteristics of pre-polymerised metal coagulants, such as polyaluminium chlorides (PACl), and to the further improvement of their properties. Various organic and inorganic additives have been introduced in the structure of the backbone chemicals to form new composite coagulants or flocculants, in order to achieve the desirable combination of higher efficiency and cost-effectiveness (Tzoupanos and Zouboulis 2008, Zhang et al. 2014b). The backbone of a new composite chemical could also be a natural compound such as starch, with modification to enhance the flocculation capacity (Wang et al. 2013). Fenton's reagent, a solution of hydrogen peroxide and an iron catalyst, has been found effective in sludge conditioning but the organic carbon content of the resulting supernatant as well as the relatively higher dosage and cost of Fenton's reagent should be taken into consideration for its ultimate application (Buyukkamaci 2004). Thus the research in the coagulation-flocculation field for sludge application is continuing, especially in optimisation of the preparation and treatment conditions and discovery of new composite materials as conditioning aids.

The ideal of dual-conditioning or use of multiple chemical additives in sludge dewatering is not relatively new. Chitikela and Dentel (1998) studied dual-conditioning of AD sludge using either ferric chloride or a cationic surfactant, hexadecyltrimethyl ammonium bromide (HDTMA), followed by a cationic polymer. They reported significant reductions in the optimal doses of these additives were observed in dual-chemical conditioning when compared to the dose requirements for either chemical when used individually. Other researchers reported positive results as well in some recent dual-conditioning studies using various combinations of conditioning aids, such polyelectrolytes of different ionic charges, inorganic and organic chemicals as well as addition of skeleton builders, as shown in Table 2.4.

Likewise, physical conditioning methods such as thermal hydrolysis, ultrasonication and microwave application as pre-treatment or combined treatment have evolved over the years to enhance the dewaterability of sludge (Yeneneh et al. 2013, Ruiz-Hernando et al. 2013, Liu et al. 2012). In contrast to the coagulation-flocculation process in chemical conditioning, these technologies generally require energy input into sludge systems to destroy the cells or change the sludge/water distribution and thus affect the sludge dewatering performance. With increasing concern of proper sludge management and implementation of stringent regulations, there is an urgent need to seek a suitable and cost-effective technology to improve sludge dewatering with a realistic concession between cost of treatment and impact on health, safety and environment.

Table 2.4 Advances in sludge conditioning aids in the past fifteen years

Conditioning aids	Sludge Samples[1]	Modes/Mechanisms	Dewaterability parameters	Results	Ref.
Synthetic Materials					
Polymeric ferric sulphate (PFS) and cationic polyacrylamide (CPAM)	AS (8.5±0.5 g/L TSS)	Charge neutralisation and bridging	CST, ZP, geometric/ rheological parameters	Improve dewaterability and increase compactness of AS flocs (optimal dosages of 6.3 g/kg PFS + 0.3 g/kg of CPAM with CST 11.03 s and ZP -1.65 mV)	(Chen and Wang 2015)
Polyaluminum chloride (PACl) and HPAC[2]	Surplus sludge from membrane bioreactor (TS 1.21±0.02%)	Charge neutralisation and bridging	ZP, SRF, turbidity of sludge supernatant	HPAC was more efficient than PACl in improving sludge dewaterability due to higher positive charge density and better bridging properties (with organic additives). Sludge flocs formed were larger and more compact.	(Zhang et al. 2014b)
Sulphuric acid and surfactant (betaine)	Thickened AS (MLSS 13.7 g/L)	Solubilisation and removal of exocellular polymer	Volume of centrifugal dewatered sludge, water content of filtered sludge	Sulphuric acid alone or together with surfactant effectively improved sludge dewaterability and settleability under optimum conditions of pH 2.5 and surfactant of 0.1 g (~73 g/kg equivalent). They solubilise and remove exocellular polymer from sludge surface and hence facilitate sludge aggregation.	(Chen et al. 2001)
Fenton's reagent, a mixture of H_2O_2 and Fe(II)	Biological sludge (TS 20010 mg/L)	Advanced oxidation and cell disruption	CST, SRF	Improved dewaterability with optimum H_2O_2 and Fe^{2+} concentrations of 6000 and 5000 mg/L respectively (~550 g/kg total equivalent), in terms of SRF. Fenton's reagent may oxidise the microbial cells leading to cell destruction with release of intercellular material.	(Buyukkamaci 2004)
Alkaline hydrolysis	SS	Cell disruption	CST, solids content, viscosity, thixotropy	Desorption of extracellular polymers and release of proteins due to alkaline treatment (0.784 to 235 g/kg or till pH 12.30) reduced the viscosity and thixotropy but increased CST and solids content.	(Erdincler and Vesilind 2000b, Ruiz-Hernando et al. 2013)

Table 2.4 Advances in sludge conditioning aids in the past fifteen years (continued)

Conditioning aids	Sludge Samples[1]	Modes/Mechanisms	Dewaterability parameters	Results	Ref.
			Natural Materials		
Prickly pear cactus, *Opuntia ficus Indica*, juice (OFIJ)	Stabilised sludge	Charge neutralisation	Turbidity of filtrate, cake dryness, SRF	OFIJ exhibits positively charged surface at pH < 4.3 with optimal dosage at 0.4 g/kg. Comparable dewaterability with those of commercial flocculants and inorganic chemicals.	(Betatache et al. 2014)
Enviro-Zyme 216, an enzyme complex, and Percol 757, a cationic copolymer[3]	ADS (TS 2.6-3.2%)	Enzymatic pre-treatment (incubated at 35 °C for 16 hours), followed by conditioning with Percol 757; solubilisation and removal of exocellular polymer	CST, solids content, filtrate turbidity, suspended solids analysis	Improved dewaterability as a result of degradation of the extracellular protein and polysaccharide (responsible for poor dewaterability) by enzymatic treatment. Solids content almost doubled when 10-15 mg/L enzyme was added (~0.3-0.6 g/kg) together with ~9-12 g/kg polymer.	(Ayol 2005)
Seawater and brine	AS (TS 23,614 mg/L)	Double layer compression and salting-out effect	Moisture content, turbidity, CST, ZP	Brine was more effective in the activated sludge conditioning than the seawater due to higher cation concentration with the highest volume ratio of brine to raw sludge at 1:1.	(Liu et al. 2011)

Table 2.4 Advances in sludge conditioning aids in the past fifteen years (continued)

Conditioning aids	Sludge Samples[1]	Modes/Mechanisms	Dewaterability parameters	Results	Ref.
Microbes, *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*	Thickened sludge (TS 2.95±0.04%)	Addition of sulphur and ferrous ions as energy substrates (shaken at 28°C and 180 r/min for 42 hours); specific mechanism was not mentioned but the sludge pH was reduced to final pH of 2.79	SRF, CST	Enhanced sludge dewaterability without reducing the organic matter which is desired for subsequent disposal or reutilisation of sludge cake.	(Liu et al. 2012)
Microbial flocculant (MBF) TJ-F1[4]	Thickened sludge (VSS/TSS 55±9%)	Adsorption and bridging	SRF, TTF	The strong adsorbability between the functional groups and bridging ability of TJ-F1 produced sludge flocs which were more compact than the original ones and hence promoted the dewaterability by expelling the water in the exterior and the interior of the sludge flocs.	(Zhang et al. 2010)
Chitosan	ADS (TS 12 g/L)	Charge neutralisation and bridging	Turbidity of supernatant, ZP	Chitosan is an effective cationic bioflocculant for ADS in either acidic or neutral conditions.	(Kaseamchochoung et al. 2006)
Graft copolymer of starch with a cationic vinyl monomer	ADS (solids content not reported)	Charge neutralisation and bridging	SRF, turbidity	The graft copolymer was superior to polyacrylamide in dewatering the sludge as the grafting of cationic monomer onto starch backbone enhanced the cationic properties and increased molecular weight of the copolymer, and thus improved its flocculation ability.	(Wang et al. 2013)
		Dual Conditioning / Skeleton Builder			
Fenton's reagent, a mixture of H_2O_2 and Fe(II)	Mixture of PS and SS (TSS 27.0-32.8 g/L)	Red mud as skeleton builder (milled and sieved to <1 mm)	SRF, CST, water content, pH	Enhance dewaterability with pH close to neutrality (optimal dosages of 31.9 g/kg Fe^{2+}, 33.7 g/kg H_2O_2 and 275.1 g/kg DS of red mud with water content of sludge cake reduced to 59.8±0.4%)	(Zhang et al. 2014a)

Table 2.4 Advances in sludge conditioning aids in the past fifteen years (continued)

Conditioning aids	Sludge Samples[1]	Modes/Mechanisms	Dewaterability parameters	Results	Ref.
Cationic polyelectrolytes, ZETAG7650 and ZETAG7501[5]	ADS (TS 1.4-1.5%)	Lignite as skeleton builder (milled and sieved to less than 3 mm)	Water removal, number of fine particles in suspension by an in situ focused beam reflectance measurement (FBRM) probe, ZP	Water removal for the lignite-conditioned flocculated sludge is significantly higher than that of the flocculated sludge due to improved permeability (from the even distribution of the porous and rigid lignite particles) in filter cake. ZP is less affected by high molecular weight polyelectrolyte.	(Thapa et al. 2009)
Alum and ferric chloride	Thickened sludge (TS 2.4-3.2%)	Wood chips and wheat dregs as skeleton builders	SRF, net sludge solid yield	Improved the dewaterability of sludge and the amenability of the resulting sludge cake for incineration and composting processes.	(Lin et al. 2001)
Alum and cationic polymer (Clarifloc 3275, Polydyne)	ADS (TS 2.08±0.01%)	Compound use of inorganic metal salt (chemical binding) and organic polymer (bridging)	CST, gas chromatography (for sulphur based volatile organic compounds)	Optimum combination of alum and cationic polymer dose gave better dewatering characteristics and less sulphur-based odour generation from dewatered sludge.	(Kim et al. 2011)
Cationic (Zetag 7587) and anionic (Praestol 2540) polyelectrolytes[6]	ADS (TS 16.60 g/L)	Compound use of cationic (charge neutralisation) and anionic polymer (bridging)	CST, SRF, water content	Dual conditioning improved dewaterability and reduce conditioner dosage with the best combination dominated by cationic polyelectrolyte (70%). In terms of addition sequence, the pre-addition of cationic polyelectrolyte improved SRF while the pre-addition of anionic polyelectrolyte improved water removal.	(Kuglarz et al. 2008)

[1]AS: Activated sludge, PS: Primary sludge. SS: Secondary sludge, ADS: Anaerobic digested sludge, TS: Total solids, TSS: Total suspended solids, VSS: Volatile suspended solids

[2]HPAC is a high performance PACl composite with high yield of Al_{13} and different organic additives; both PACl and HPAC contain 10% Al_2O_3 and were produced by Beijing Wanshui Water Cleaning Agent Co., China

[3]Enviro-Zyme 216 is an enzyme product, from Winston Company, Inc., Tulsa, U.S., which contains protease, lipidase, anaerobic bacteria, Aspergillus oryzae, and an enzyme complex mixture of other hydrolytic enzymes; Percol 757 is a high molecular weight, cationic copolymer consisting of 65% acrylamide monomer and 35% acryloyloxyethyl trimethylammonium chloride

[4]Produced by Proteus mirabilis TJ-1 screened out from the activated sludge

[5]Copolymers of polyacrylamide and quaternised N,N-dimethylaminoethyl acrylate methylene chloride, produced by Ciba Specialty Chemicals

[6]Zetag 7587 is polyacrylamide based, high molecular weight, cationic charge polymer; Praestol 2540 is polyacrylamide and sodium acrylate based, medium molecular weight, medium anionic charge polymer.

2.14 Conclusion

Application of conditioning aids to enhance dewatering is inevitable in wastewater sludge processing. With the ever-increasing sludge production and the growing awareness from the public and regulating authorities, conditioning aids have undergone significant evolution from the time they were first introduced. At present, polymer conditioning has become the most dominant form of sludge conditioning in most WWTPs. Knowledge and research about sludge characteristics, influencing factors and mechanisms of conditioning mechanisms as presented in this chapter have enabled the introduction of various sophisticated treatment processes and ongoing trials of novel conditioning materials and state-of-the-art technologies in sludge dewatering. Comprehensive measurement techniques using both dewaterability and rheological parameters are highly recommended as they can generate important data for the selection of operational parameters and chemical dosage. This chapter provides information on how sludge dewatering operation can be optimised through some cost-effective, process-efficient, and environmentally friendly approaches, accompanied by reliable parameter measurement and control of conditioner dosage. With this literature background, the use of the natural biopolymer, chitosan, is identified as the potential conditioning aid commendable for sludge dewatering. The following chapter provides the experimental procedures to test the feasibility of chitosan together with the other conditioning chemicals in optimising the sludge dewatering performance under the influencing physicochemical process parameters.

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CHAPTER 3

MATERIALS AND METHODS

This chapter describes the research methodology used in this study which can be divided into three parts. The first part describes the collection of anaerobic digested sludge samples, the formulation of synthetic sludge, and the preparation of conditioning chemicals. The second part explains the conditioning experiments as well as the detailed analytical procedures for sludge characteristics and dewaterability. Specific measurements include capillary suction time, specific resistance to filtration, zeta potential, turbidity, Fourier Transform Infrared spectrum, particle size and microscopic imaging. The last part of this chapter introduces the rheological rotational test on sludge under the effect of chemical conditioning.

3.1 Materials

3.1.1 Collection of anaerobic digested sludge sample: the Beenyup WWTP

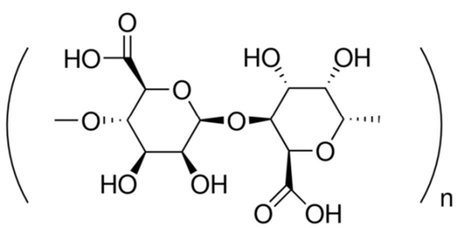
The anaerobic digested sludge samples were obtained from the Beenyup Wastewater Treatment Plant (WWTP) of Water Corporation in Perth (see Figure 3.1(a)). The treatment plant used an advanced secondary treatment process combining a conventional activated sludge process with biological nutrient removal. The sludge treatment facilities consisted of three main sections, i.e., sludge digestion, gas system, and sludge dewatering and disposal. The two-stage heated anaerobic digesters received a blend of primary sludge and excess activated sludge after dissolved air flotation thickening (DAFT). Sludge temperature in the digesters was maintained at 35°C in the mesophilic range for the optimum bacterial digestion of sludge and production of methane gas as fuel for heating and mixing requirements. All digested biological sludge samples were stored at 4°C to minimise microbiological decomposition and were discarded after 1 week.

(a) Anaerobic digested sludge (b) Synthetic sludge

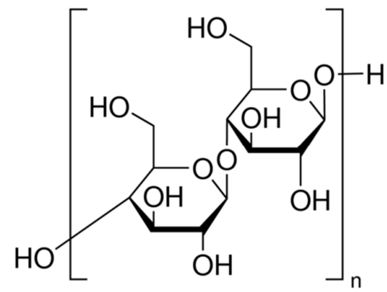
Figure 3.1 Sludge samples used in this study

3.1.2 Preparation of chemicals and synthetic sludge

A chemically well-defined synthetic sludge was applied in this study for further conditioning studies and analysis due to the concerns of variation in sludge characteristics and prevention of possible biological hazard in analytical laboratory. The synthetic sludge formulation was carried out as per Dursun (2007) to simulate anaerobic digested sludge for this work. Five chemicals used in the preparation, namely sodium alginate, cellulose, yeast, potassium chloride (KCl) and calcium chloride ($CaCl_2$) were purchased from Sigma-Aldrich. The polysaccharide sodium alginate (A2158, Sigma), also known as alginic acid sodium salt, was derived from brown algae, and was used to simulate microbial extracellular polymeric substances (EPS). Both microcrystalline cellulose (310697, Aldrich) and medium fibrous cellulose (C6288, Sigma) were studied for their application as a filamentous backbone structure in synthetic sludge. Chemical formulas of alginate and cellulose are shown in Figure 3.2. Yeast from *Saccharomyces cerevisiae* (YSC2, Sigma) was used to simulate the microorganism or bacteria while potassium and calcium ions of common laboratory reagent grade were used as bridging ions. The formulation aims to produce a synthetic sludge system comprising a gel or polymeric fraction (by addition of alginate and bridging ions) and a particulate or structural fraction (by addition of cellulose and yeast) (Dursun 2007).



(a) Alginate



(b) Cellulose

Figure 3.2 Chemical formulas of the two polysaccharides used in synthetic sludge formulation (Sigma-Aldrich.com)

To prepare 5 g/L alginate stock solution, 5 g alginate powders were weighed onto a weighing paper using an analytical balance (Sartorius BSA224S-CW). The weighed alginate powders were dissolved with distilled water in a 1-L beaker by adding them slowly into a vortex created by 400-rpm stirring using an IKA magnetic stirrer (IKA RCT basic, safety control) to avoid agglomeration. The stirring was continued for 1 hour to completely dissolve alginate. The alginate solution was then transferred into a 1-L volumetric flask to make up a 1-L solution. 2 M KCl and 0.05 M $CaCl_2$ were prepared as standard solutions by dissolving the weighed amount of chemicals in a small amount of distilled water in a small beaker, followed by transfer to a 1-L volumetric flask to make up a 1-L solution each.

According to the procedure outlined in Dursun (2007), 16.6 g cellulose and 7.3 g yeast were weighed and added into 540 mL of 5 g/L alginate solution in a 1-L beaker. Distilled water was then added to the mixture to a total volume of about 700 mL. The mixture was mildly stirred at 150 rpm for 2 hours to allow attachment of alginate onto the surface of cellulose and yeast particles. The mixture was occasionally stirred with glass rod to keep settled particles in suspension. After 2 hours stirring, 91 mL of 2 M KCl solution was added to the mixture and stirred at 300 rpm for 2 minutes, followed by addition of 200 mL of 0.05 M $CaCl_2$ solution stirred at 500 rpm for 3 minutes. The resulting suspension was then washed with distilled water at a volume ratio of 3:1 (water:suspension) to reduce the high salt concentration and was left to settle for 2.5 hours. A dense layer of slurry was observed at the bottom of the final suspension whilst the top layer was a turbid supernatant which was removed via siphon action to reduce the suspension to 1 L of standard synthetic sludge with total solids of about 22±1 g/L.

The sludge was diluted with the supernatant instead of distilled water to the desired total solids in order to maintain the conductivity of synthetic sludge close to the one of anaerobic digested sludge. The volume of dilution water, V_{DW} added was calculated using Equation 3.1.

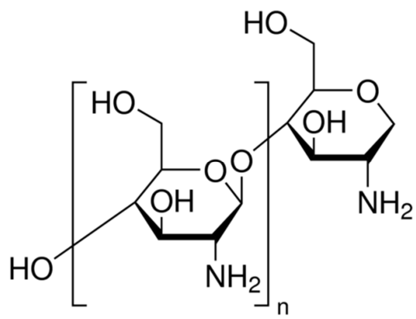
$$V_{DW} = V_0\left(\frac{TS_0 - TS}{TS - TS_S}\right) \qquad (3.1)$$

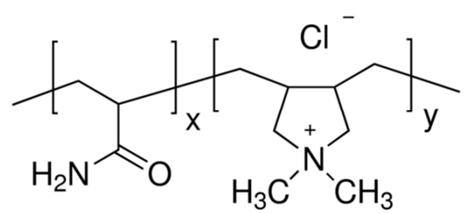
where V_0 is the volume of standard sludge before dilution, TS_0 the total solids of standard sludge before dilution, TS the desired total solids after dilution, and TS_S the total solids of supernatant. The desired total solids after dilution were of the average of 15.5 g/L or 1.55%. The resulting synthetic sludge was a turbid and milky suspension as shown in Figure 3.1(b).

3.1.3 Preparation of organic conditioning chemicals

A low molecular weight chitosan (448869, Aldrich) was used as the major organic conditioner in this study which was obtained from Sigma-Aldrich, USA. Based on the product information from Sigma-Aldrich.com, this chitosan was 75-85% deacetylated with molecular weight of 50,000–190,000 Daltons based on viscosity 20-300 cP at 1% chitosan in 1% acetic acid. A medium molecular weight chitosan of 190,000–310,000 Da (448877, Aldrich) was obtained as well to examine the effect of molecular weight. Chitosan is a type of cationic biopolymer which is also referred to as organic polyelectrolyte. They dissociate upon addition to acidic aqueous solution into positively and negatively charged species which increase the conductivity of the solution. The positively charged species was desired in this work to promote destabilisation of sludge through charge neutralisation. Figure 3.3(a) shows the chemical formula of chitosan.

Chitosan is supplied in the form of powders, and is insoluble in water or organic solvents. To prepare 1% chitosan solution by weight, 1 mL acetic acid of analytical reagent grade (Hamburg Chemical GmbH), was first pipetted into distilled water in a 100-mL volumetric flask using a micropipette (100–1000 μL, Eppendorf Research plus) to make up a 100-mL solution of 1% acetic acid. 1 g chitosan was then weighed and added to the 100-mL solution of 1% acetic acid in a 250-mL reagent bottle with blue screw cap. The solution was stirred at 100 rpm for 30 minutes to completely dissolve chitosan. The resulting chitosan solution was viscous and was used immediately within 2 weeks.





(b) PAC

(a) Chitosan

Figure 3.3 Chemical formulas of the polymeric conditioning chemicals (Sigma-Aldrich.com)

Several other cationic organic polymers were studied as well to examine the effect of conditioner type in sludge conditioning and dewatering. A commercial polyacrylamide copolymer, namely poly(acrylamide-co-diallyldimethylammonium chloride) (409081, Aldrich, abbreviated as PAC in this study), was purchased from Sigma-Aldrich as a 10% solution by weight. This polymer comprised about 55% acrylamide by weight (see Figure 3.3(b)). Another commercial polymer, EMA 8845 MBL (SNF, Australia), was a generous gift from the Beenyup WWTP and it was supplied as a cationic water-soluble polymer after dilution of about 0.65% by weight. These organic chemicals were used as received.

3.1.4 Preparation of inorganic conditioning chemicals

The inorganic conditioners used in this study were from the laboratory reagent grade chloride salts of sodium, potassium, magnesium, calcium, aluminium and ferric. To prepare 1% stock solution of each chloride salt, 1.0 g chloride salt was weighed and dissolved with distilled water in a 100-mL volumetric flask to make up a 100-mL solution. The solution was then transferred to a 100-mL reagent bottle for immediate use.

3.2 Characterisation of Sludge

The characteristics of the sludge sample were determined according to Standard Methods 2540 (APHA 2012) for the total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS); Standard Methods 2710F for the specific gravity (SG) as well as the Reactor Digestion Method (Hach Method 8000, adapted from Standard Methods 5220D) for Chemical Oxygen Demand (COD) test.

3.2.1 Total solids (TS)

The measurement method applies the principle of increase in weight over that of an empty dish after evaporation at 103–105°C. To do so, a clean evaporating dish was first heated at 103–105°C in a Memmert drying oven for 1 hour and stored in a desiccator until needed. The dish was weighed immediately before use. 5-mL well-mixed sludge sample was pipetted to the prepared dish. The dish with sample was dried in the oven at 103–105°C for 2.5 hours to obtain a constant weight. After drying, the dish was cooled in the desiccator and weighed. The TS content expressed in g/L was then calculated using Equation 3.2.

$$\text{TS} = \frac{(W - W_0)\times 1000}{V_s} \tag{3.2}$$

where W is the weight of dried residue and dish (g), W_0 the weight of empty dish (g), V_s the volume of sludge sample (mL) and the conversion factor 1000 mL/L. All samples were analysed in duplicate.

3.2.2 Total suspended solids (TSS) and total dissolved solids (TDS)

For the measurement of TSS and TDS, a well-mixed sample was filtered through a standard glass fibre filter and the residue retained on the filter was dried at 103–105°C for TSS whilst the filtrate was dried at 180°C for TDS. To conduct the experiment, the filtering apparatus was assembled with a Whatman glass fibre filter paper seated in a Buchner funnel with applied vacuum to the filtering flask. The filter paper was washed with three successive 20-mL volumes of reagent-grade water with extended suction to remove all traces of water. The filter paper was then transferred to an inert aluminium weighing dish as a support, dried in the oven at 103–105°C for 1 hour and stored in a desiccator until needed. The filter paper was weighed immediately before use. 2.5-mL of the well-mixed sludge sample was pipetted onto the seated filter paper on the filtering apparatus. The sample on the filter paper was washed with three successive 10-mL volumes of reagent-grade water with suction for about 3 minutes after filtration was complete. The loaded filter paper was transferred to the aluminium weighing dish and dried in the oven at 103–105°C for 2.5 hours until a constant weight was obtained. After drying, the filter paper was cooled in the desiccator and weighed. Similar to Equation 3.2, the amount of TSS expressed in g/L was calculated using Equation 3.3 where the sample was weighed on the filter paper rather than the dish.

$$\mathrm{TSS} = \frac{(W - W_0) \times 1000}{V_s} \tag{3.3}$$

where W is the weight of dried residue and filter paper (g), W_0 the weight of filter paper (g), V_s the volume of sludge sample (mL) and the conversion factor 1000 mL/L.

For determination of TDS, a clean evaporating dish was first heated at 180°C in the drying oven for 1 hour and stored in a desiccator until needed. The dish was weighed immediately before use. The total filtrate with washings from the previous TSS determination was transferred to the weighed dish and dried in the oven at 180°C for 2.5 hours to obtain a constant weight. After drying, the dish was cooled in the desiccator and weighed. Similarly, the TDS (g/L) was calculated using Equation 3.4.

$$\text{TDS} = \frac{(W - W_0) \times 1000}{V_s} \tag{3.4}$$

where W is the weight of dried residue and dish (g), W_0 the weight of dish (g), V_s the volume of sludge sample (mL) and the conversion factor 1000 mL/L. All samples were analysed in duplicate.

3.2.3 Specific gravity (SG)

The SG of the sludge was determined by comparing the mass of a known sludge sample volume at a specific temperature to the mass of the same volume of distilled water at 4°C (APHA 2012). The sludge sample temperature was recorded for determination of correction factor. An empty 10-mL graduated cylinder was weighed. The cylinder was filled with 10-mL sludge sample and weighed. Next the cylinder was filled with 10-mL water and weighed. Equation 3.5 was used to calculate the SG value.

$$\text{SG} = \frac{(S - W)}{(R - W)} \times F \tag{3.5}$$

where S is the weight of sludge sample and cylinder (g), W the weight of empty cylinder (g), R the weight of water at 4°C (g) and the temperature correction factor F taken from APHA (2012).

3.2.4 Chemical oxygen demand (COD)

The COD principle infers that the dichromate ion oxidises COD material in a sample during digestion which results in the change of chromium from the hexavalent (VI) state to the trivalent (III) state (APHA 2012). These ions absorb in the visible region of the spectrum which can be measured and expressed as the COD value in mg/L. This study applied the Reactor Digestion method (Hach Method 8000) for determination of high range COD which is approved by USEPA for wastewater analysis (Water Analysis Handbook 2014) . The method is based upon the oxidation of organic matter using acid dichromate solution followed by spectrophotometric determination

The high range COD digestion reagent vials (0–1500 mg/L, Hach) were used in this study. Prepared COD reagents in vials eliminated the need for measurement of corrosive and toxic chemicals such as the concentrated sulphuric acid and mercury sulphate. When the COD exceeded 1500 mg/L, the sample was diluted to bring the results in range. 0.20-mL of a well-mixed sludge sample was pipetted into the vial held at an angle of 45°. Blank sample was prepared using deionised water. The vial was capped and inverted gently for a few times to ensure proper mixing. The vial was heated in a digital block heater (WiseTherm HB-48, Wisd) at 150°C for 2 hours. After heating, the power was switched off and the vial was left cooled in the heater for approximately 20 minutes to 120°C or less. The vial was then inverted for a few times and placed in a tube rack to cool to room temperature. The blank sample vial was wiped clean and inserted into the cell holder of a Hach DR 2800 Portable Spectrophotometer to be set as a reference point for 0 mg/L COD. Subsequently the sample vial was wiped clean and inserted into the cell holder of the spectrophotometer for measurement. The meter display gave the reading of COD in mg/L.

3.3 Conditioning Experiments

The effects of conditioner dosage and type, pH, temperature, mixing speed and mixing time on sludge dewatering performance were studied by batch conditioning experiments. A series of 250-mL beakers were set up similar to the jar test but in a smaller volume to simulate a mixing, flocculation, and settling cycle. A 100-mL aliquot of sludge sample was added to each beaker which was then placed on an IKA magnetic stirrer (IKA RCT basic, safety control) for the mixing process. All sludge samples were brought to room temperature and were gently agitated before each test to ensure a representative measurement.

The conditioner solution was pipetted into the 100-mL sludge sample using an adjustable pipette (1–10 mL, Eppendorf Research plus) at the predetermined dosage, expressed as the weight of conditioner over the weight of total solids in the sludge (g/kg). The required volume of conditioner was calculated using the dosing formula from Equation 3.6.

$$V_C = \frac{TS \times V \times D_C}{C_C \times 1000} \tag{3.6}$$

where V_C is the dosing volume of conditioner (mL), TS the total solids of sludge sample (g/L), V the volume of sludge sample (mL), D_C the desired dosage (g/kg), C_C the conditioner concentration (g/L), and the conversion factor 1000 g/kg. The conditioner was gradually dosed into the sludge sample within 30–60 s to ensure uniform dispersion. The conditioned sludge was then rapidly stirred at 300 rpm for 60 s to aid the coagulation. Subsequently, the mixing was reduced to 50 rpm for 300 s to promote flocculation. These mixing conditions were used in all experiments except for the study of the effects of mixing speed and mixing time during the flocculation step (slow mixing). To study the effect of dual-conditioning, the sludge was conditioned with simultaneous addition of organic and inorganic conditioners under the similar mixing conditions.

The pH of sludge sample was adjusted using either 0.5 M hydrochloric acid (HCl) or 0.5 M sodium hydroxide (NaOH). Such concentrations were applied to minimise sample volume variation after pH adjustment. All experiments were conducted at room temperature 24±2°C except for the study of temperature effect which was conducted using a water bath as shown in Figure 3.4. During the experiments, pH, electrical conductivity (EC), and temperature were measured directly on the sludge with a Multi-Parameter Meter (Hach sensION+ MM150). The dewatering performance of the conditioned sludge was assessed at the end of mixing.

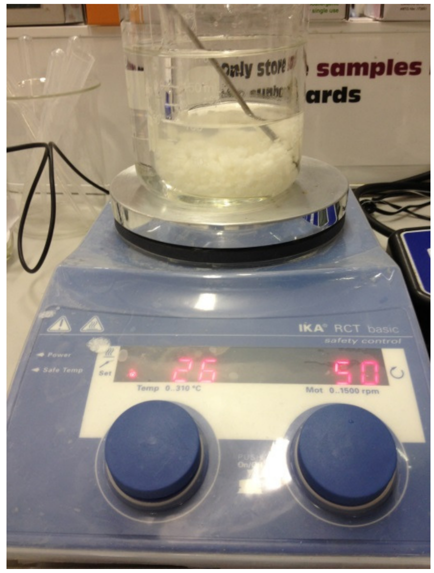
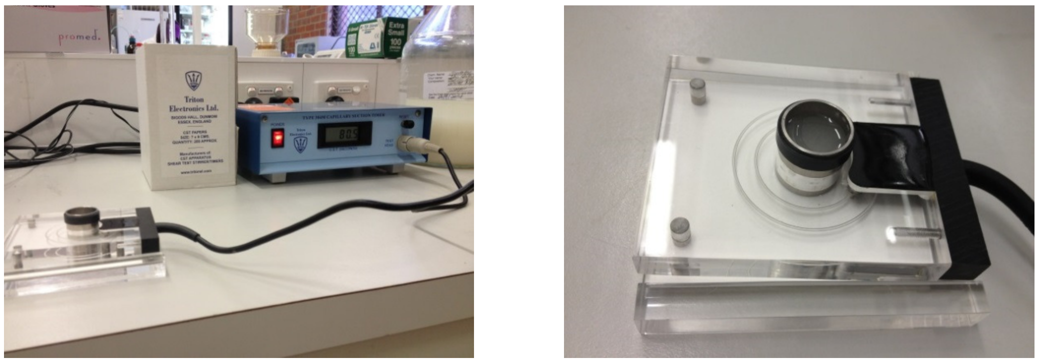


Figure 3.4 Set-up of a 250-mL jar test beaker in water bath

3.4 Analysis of Sludge Dewaterability

3.4.1 Capillary suction time (CST) test

Dewaterability of sludge is most often quantified by measuring CST according to Standard Methods 2710G (APHA 2012). CST test was conducted using a CST apparatus purchased from Triton Electronics Ltd., UK. To operate the apparatus, the test-head assembly was first plugged in the digital timer as shown in Figure 3.5(a). The meter was turned on and reset. A standard CST chromatography paper was placed onto the lower base block and the upper electrode block was placed onto the paper, ensuring the electrode points contact the paper evenly. A 1.8-cm funnel was used as the sludge was considered slow filtering at the order of 10^2 s with respect to solids content of 1.5% according to the CST Equipment Manual (Manual 1998). The funnel was inserted into the electrode block and seated with slight pressure and a quarter turn to prevent surface leaks. The amount of sample introduced into the funnel is not critical as long as there is sufficient to complete the test as the capillary suction pressure generated by the filter paper is much greater than the hydrostatic head in the funnel (CST Equipment Manual 1998). In this study, a representative sludge sample of about 5 mL was transferred into the test funnel using a disposable transfer pipette. Figure 3.5(b) illustrates a 1.8-cm funnel filled with the sludge sample. The CST paper drew liquid from the sludge by capillary action. Time measurement automatically started once the liquid reached the inner contact point and ended when the outer contact point was reached. CST reading was displayed on the digital timer in the unit of seconds (s) and recorded manually.



(a) Electrode block connected to timer (b) Funnel filled with sample

Figure 3.5 Set-up of capillary suction time test

3.4.2 Specific resistance to filtration (SRF) test

The rate of water removed during filtration dewatering is usually determined as the SRF. The SRF test was conducted using a simple laboratory filtration system as described by Novak (2001). A Buchner funnel was assembled onto a modified graduated cylinder with glass hose connection to a vacuum pump and gauge as shown in Figure 3.6. The vacuum gauge was set to the gauge pressure of –385 mmHg which is equivalent to the absolute pressure of 50 kPa. The volume of filtrate collected within the graduated cylinder was then timed with a stopwatch. The data was then used to determine SRF (m/kg) using Equation 3.7.

$$\mathrm{SRF} = \frac{2A^2 \Delta P b}{\eta w} \tag{3.7}$$

where A is the filtration area (m^2), ΔP the applied vacuum pressure (N/m^2), η the dynamic viscosity (kg/m.s) and w the weight of dry cake per unit volume of total filtrate collected at the end of filtration (kg/m^3). The coefficient b (s/m^6) was obtained from the initial linear slope of the plot of the time of filtration to volume of filtrate ratio (*t/V*) versus *V* itself. The filtered sludge cake retained on the filter paper was used to determine the cake solids content following filtration dewatering. This was done by overnight heating in oven at 103–105°C and the percentage of cake solids content was then calculated using Equation 3.8.

$$\text{Cake solids content} = \frac{W_2 - W_0}{W_1 - W_0} \times 100 \tag{3.8}$$

where W_2 is the weight of dried cake and paper, W_0 the weight of filter paper, and W_1 the weight of wet filtered cake and paper. Example of SRF and cake solids content calculation is given in Appendix A.1.

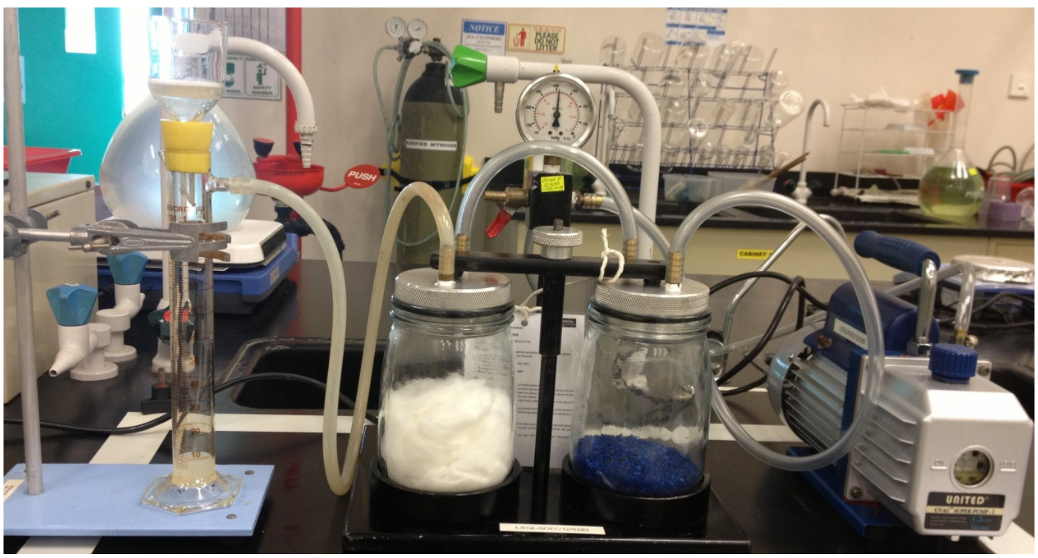


Figure 3.6 Set-up of filtration system for the specific resistance to filtration test

3.4.3 Turbidity

Turbidity of supernatant was measured after 30 minutes sludge settling using a Hach 2100Q turbidimeter. The prepared supernatant sample was pipetted into the designated sample cell. The meter was turned on. The sample cell holder lid was opened to insert the cell and then closed for measurement. The *Read* button was pressed and the display showed the result. This instrument measured turbidity from 1 to 1000 NTU. To predict the out-of-range reading for very turbid supernatant, Equation 3.9 was developed based on the calibration by dilution of sludge with known concentration. Detailed description of calibration can be found in Appendix A.2.

$$T = 2^n (T_0 + 20.1) - 20.1 \tag{3.9}$$

where T is the calibrated turbidity, n the number of dilution, T_0 the turbidity after dilution and the constant 20.1 was obtained from the calibration curve in Figure A.2 of Appendix A.

3.4.4 Zeta potential

Zeta potential (ZP) measurement was performed on the supernatant after the conditioned sludge suspension was allowed to settle for a period of 30 minutes. Zetasizer Nano ZS (Malvern) was used to measure ZP between the particle surface and the dispersing liquid (also called the slipping plane) using Laser Doppler Electrophoresis method which is a combination of Electrophoresis and Laser Doppler Velocimetry techniques (see Figure 3.7). The instrument measures the movement of a particle (i.e. its velocity) in a liquid when an electrical field is applied where the electrophoretic mobility data is converted into ZP value using the Henry equation (Zetasizer Nano User Manual 2013).

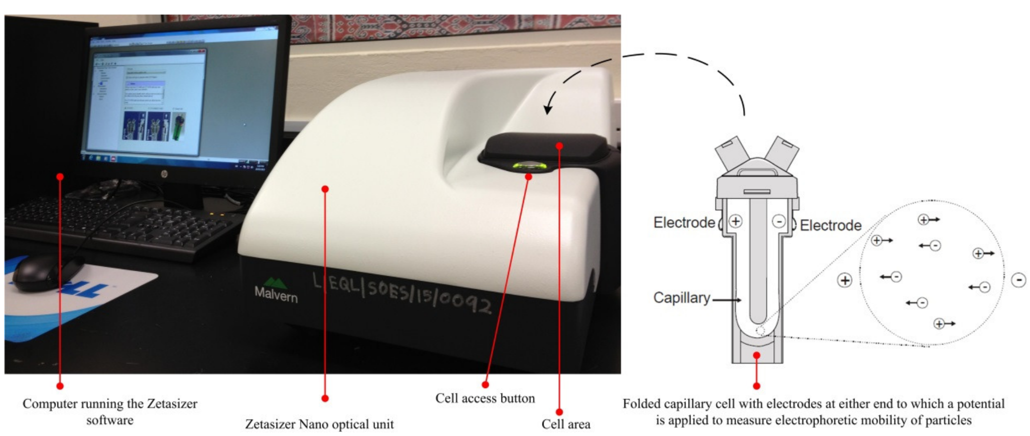


Figure 3.7 Zetasizer and folded capillary cell for zeta potential measurement

To make the measurement, the instrument was turned on and the Zetasizer software was started. The prepared supernatant sample was injected into a clean folded capillary cell (DTS1070, Malvern) using a plastic syringe until it filled up to the marker, and the cell openings were stoppered. A Standard Operating Procedure (SOP) measurement file was programmed and opened in the software. When prompted by the software, the cell access button on the instrument was pressed to open the lid and the cell was inserted into the cell holder. The cell lid was closed and the measurement was started by clicking the *Start* button in the software. After the measurement was completed, the result was displayed and saved.

3.4.5 Fourier Transform Infrared (FTIR) spectrum

The Fourier Transform Infrared (FTIR) spectrum of the sludge was analysed with a FTIR spectrometer (PerkinElmer Spectrum 100) fitted with the Universal Attenuated Total Reflectance (ATR) sampling accessory as shown in Figure 3.8. This sampling technique is non-destructive and is ideal for analysing solids, powders, pastes, gels, liquids and solutions. It is also useful in measuring homogeneous solid samples, solid surfaces and coatings on solid samples (Universal ATR Sampling Accessory User's Guide 2008). The technique involves placing a sample on top of a crystal with a high refractive index where an infrared beam is passed into the accessory from the instrument and up into the crystal. The incident beam hits the sample surface and propagates by total internal reflection in the crystal, and back towards a detector within the instrument. A controlled force is often applied to ensure good contact between the sample and the surface of the crystal to prevent loss of beam penetration.

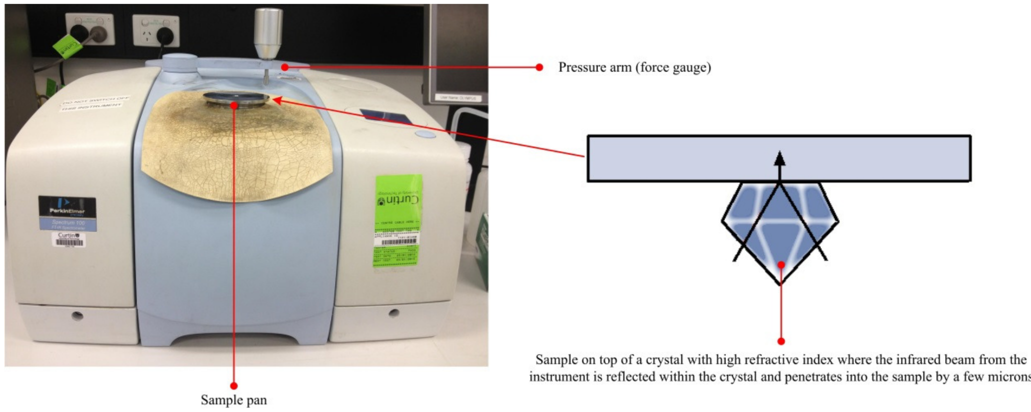


Figure 3.8 Universal ATR Sampling Accessory and principle for FTIR spectrum measurement

To perform a FTIR spectrum measurement, the spectrometer was connected to a computer and the scan was conducted using commands in the Spectrum software. Once the software was logged in, a background spectrum was first collected by selecting *Instrument* > *Scan* > *Background*. The sludge sample was then placed on the sample pan and the force gauge was applied as indicated in the software using the monitor button. The scan was started and the raw spectrum was obtained. The sample was removed immediately and the sample pan was cleaned. ATR correction was applied to the raw spectrum by selecting *Process* > *ATR Correction* on the software and the desired spectrum was obtained.

3.4.6 Floc size and structure

As given in Figure 3.9, a Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK) was used to measure the size of the sludge flocs formed after conditioning. The Mastersizer 2000 uses the principle of laser light scattering to measure the size of particles. As a laser beam passes through a dispersed particulate sample, the intensity of light scattered is measured and this data is then analysed to calculate the size of the particles based on the correspondence relationship between particle size and light intensity distribution pattern using the Mie scattering theory applied within the instrument software. Since the size distribution is based on the volume, the average floc size is quoted as the volume weighted mean diameter in this work.

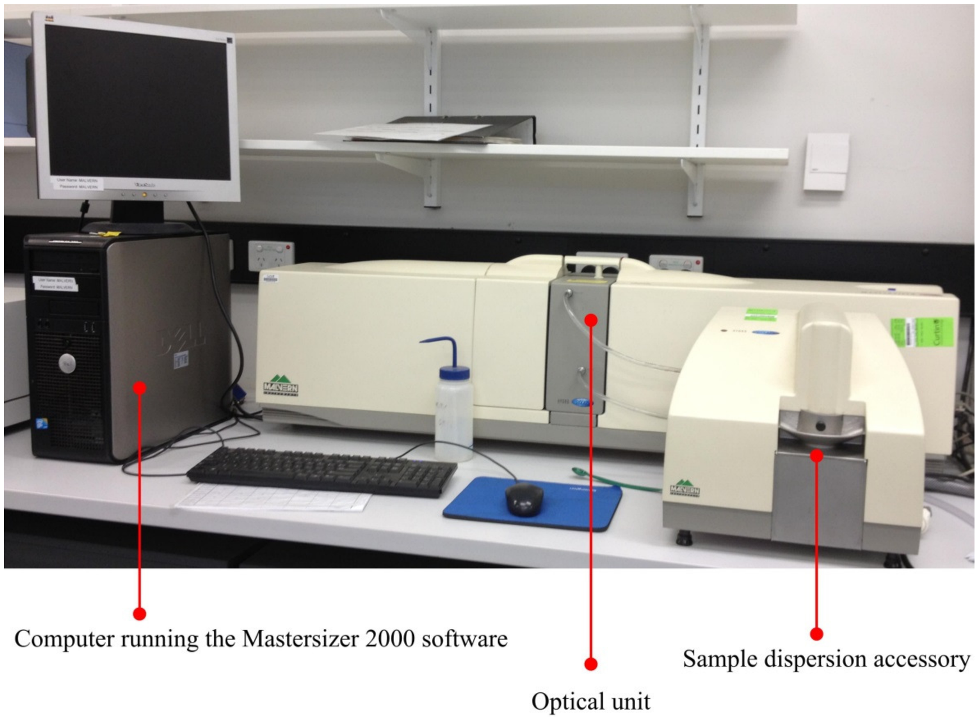


Figure 3.9 Malvern Mastersizer 2000 for particle size measurement

To begin with, the system was switched on and the Mastersizer 2000 software was opened. A SOP was programmed and started by selecting *Measure* > *Start SOP*. Following the dialogue in the software, the SOP measurement ran automatically by cleaning the tank, measuring an electrical background, aligning the optical system and measuring the optical background. When the *Add sample* tab appeared, the sample was slowly dispersed in water into the sample dispersion accessory (and hence into the tank) until the *Laser Obscuration* bar showed green in the software. The obscuration measured the fraction of light "lost" from the analyser beam when the sample was introduced. Once enough amount of sample was added, the *Start* button was pressed and the sample was measured. The measurement result on size distribution was saved for further analysis.

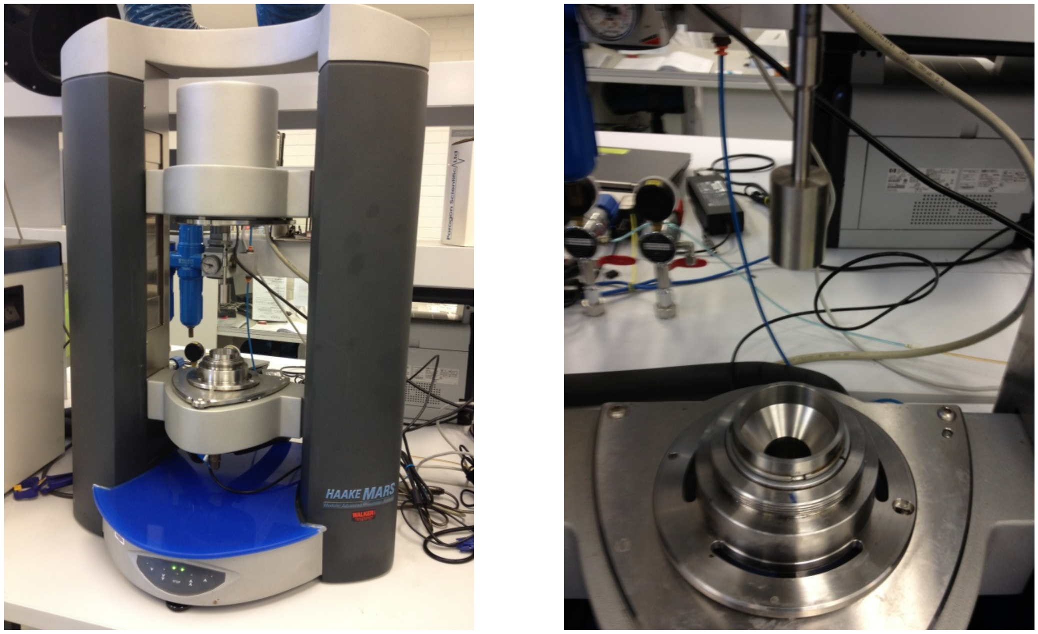
For the study of floc structure, a Variable Pressure Scanning Electron Microscope (VP-SEM, Zeiss) was used to scan the sample with a focused electron beam and obtain images about the samples' topography with high resolution surface information. The sludge sample was filtered with filter paper and examined directly in wet condition under the microscope imaged at 100× magnification, 15.0 kV. In addition, microscopic image analysis was also performed on the sludge sample using a Nikon Eclipse 50i microscope. The scale was calibrated by a micrometer with 4×10 magnification give 25 μm per sub-division, 10×10 give 10 μm per sub-division, 40×10 give 2.5 μm per sub-division.

3.5 Application of Rheological Tool for Dewaterability Analysis

Chemical conditioning affects sludge rheological properties. In this section, sludge rheology was measured to yield the desired rheological parameters including viscosity, yield stress and rheogram peak. The results were correlated to sludge dewaterability for determination of optimum conditioning parameters such as chemical dosage, pH and temperature.

3.5.1 Rheological measurements

Rheological tests were carried out in controlled shear rate mode using a HAAKE MARS II modular advanced rheometer system (Thermo Scientific) (see Figure 3.10(a)). As depicted in Figure 3.10(b), the measuring geometry used was a coaxial cylinder (also known as concentric cylinder) (20 mm in diameter, ISO 3219, Type Z20 DIN) with gap 4.2 mm. The gap size was decided based on the recommendation from Ratkovich et al. (2013) that it should be larger than the biggest floc particle but as small as possible to minimise correction factors and avoid eddies formation (turbulence).



(a) (b)

Figure 3.10 Rheological measurement using (a) HAAKE MARS rheometer and (b) concentric cylinder as measuring geometry

To operate the instrument, the pressure valve and heater were first turned on. The rheometer was connected to a computer and the measurement was conducted using commands in the RheoWin3 Job Manager software. The measurement protocol was saved as Saved RheoWin Job in the software. When opened, the measuring geometry automatically moved to the measurement position, and then to zero position before it was lifted apart. The *Load Sample* dialogue appeared in the software. About 8 mL of the sludge sample was pipetted into the measuring cylinder. The measurement was started. In this work, the sample was subjected to a controlled ramping of shear rate from 0.0001 to 100 s^{-1} in 300 s. The temperature of the sample in the rheometer was maintained at 25°C in all measurements except for the study of temperature effect. The HAAKE RheoWin 3 software was used to record the rheogram data which was later exported to Microsoft Excel 2010 software for further analysis.

3.5.2 Rheological models

The development of sludge rheological models was studied under different experimental conditions. For non-Newtonian, shear thinning fluids, depending on the presence of a yield stress, the power-law model (or Ostwald model) (Equation 3.10) and Bingham model (Equation 3.11) were used to fit the data in the sludge rheogram (plot of shear stress against shear rate) wherever applicable, as they are identified as the most basic and common rheological models used (Eshtiaghi et al. 2013).

$$\tau = K\dot{\gamma}^{m} \tag{3.10}$$

$$\tau = \tau_0 + \eta\dot{\gamma} \tag{3.11}$$

where τ is the shear stress (Pa) and $\dot{\gamma}$ the shear rate (s^{-1}). For the power-law model, K is the consistency index and m is the shear thinning index where $m < 1$. On the other hand, the yield stress τ_0, is incorporated in the Bingham model. The best-fit model was determined by the correlation coefficient of R^2 which was computed using the *Analysis* tab under *Chart Tools* in Microsoft Excel software.

3.5.3 Rheological parameters in optimisation of sludge dewaterability

High-shear rate viscosity, yield stress and rheogram peak height were studied for their feasibility as rheology tools to optimise chemical dosage and sludge dewaterability. The non-Newtonian sludge exhibited change in viscosity with shear rate. From the rheogram data, the viscosity-shear rate curves were plotted to examine the change in apparent viscosity and to determine the high-shear rate viscosity where the differences in viscosity became negligible. Meanwhile the yield stress values were determined directly from the best-fit Bingham equation or by simple extrapolation of rheogram at low shear rates if none of the model fitted the data. The initial peak appeared in the rheogram was taken as another parameter to determine optimal sludge conditioning. This peak corresponded to a zero derivative in the rheogram. The readings of these rheological parameters were used in parallel with CST as control parameters for optimisation of process parameters undertaken in this study.

3.6 Conclusion

The effect of chemical conditioning under various physicochemical process parameters was studied for the resulting sludge dewaterability and rheological behaviour as described in this chapter. The overall research methodology is summarised in Figure 3.11 for a quick reference. The findings from this study are presented separately in the following four chapters.

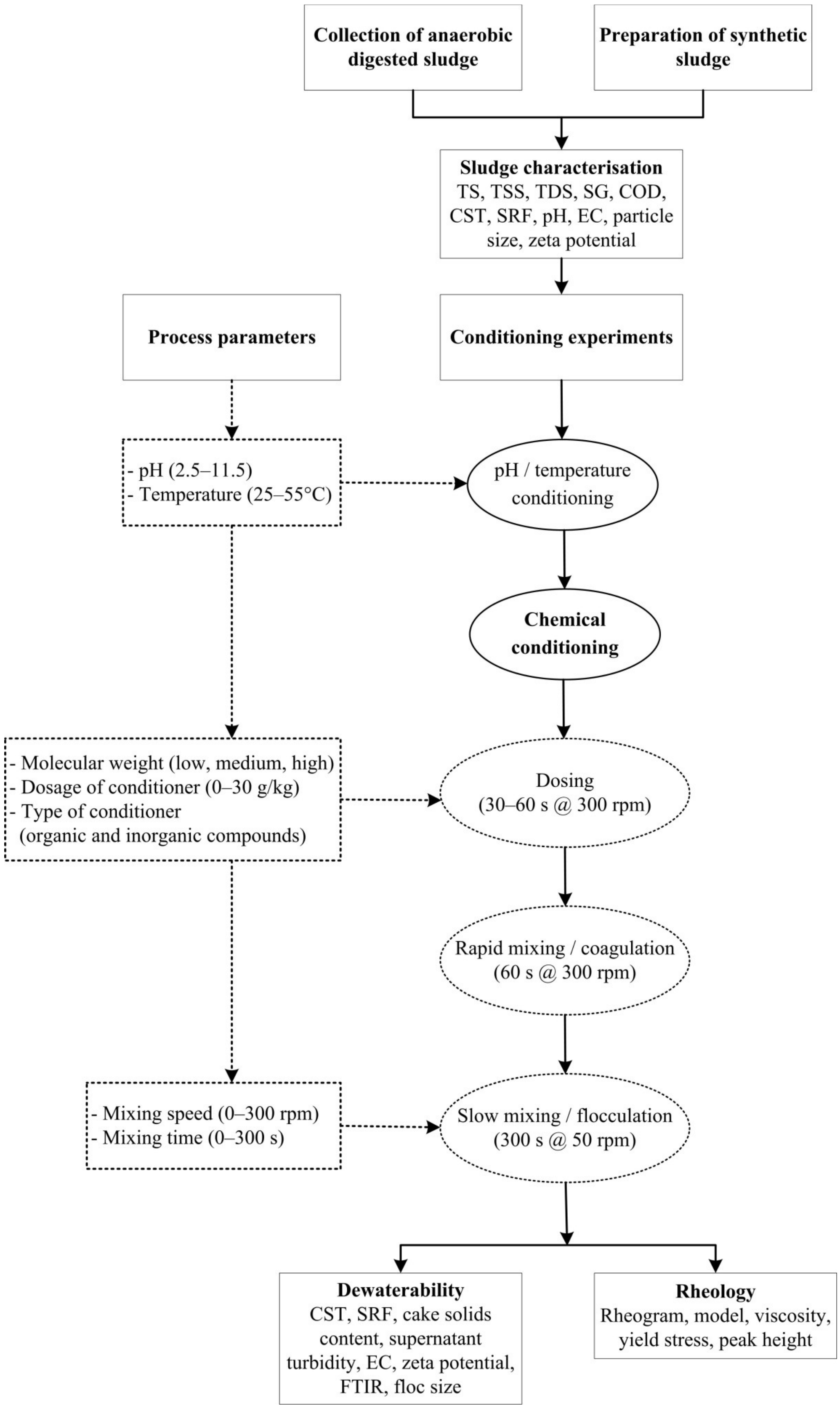


Figure 3.11 Flowchart of research methodology

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CHAPTER 4

CHARACTERISATION AND MODIFICATION OF SLUDGE

4.1 Introduction

The nature of sludge is complex with wide variation in its physical, chemical and biological properties. Sludge characteristics change instantly with time, temperature and its surrounding environment. It is therefore difficult to carry out controlled experiments in sludge studies. In the past twenty years, several researchers have pointed out a clear need for a chemically well-defined, stable and representative sludge surrogate to study sludge dewatering, settling and conditioning characteristics (Sanin and Vesilind 1996, 1999, Örmeci and Vesilind 2000, Chu and Lee 2005, Sawalha and Scholz 2007, Nguyen et al. 2007, Nguyen et al. 2008a, b, Wang et al. 2012). This chapter presents the preliminary findings and discussion of sludge characteristics and the subsequent modification to the synthetic sludge used in this study in order to simulate some important physical and chemical properties of anaerobically digested (AD) sludge in relation to conditioning and dewatering. Factors affecting the response of synthetic sludge in dewatering performance were discussed with regard to the change in synthetic sludge formulation. The modified sludge was further analysed to better understand its morphology, chemical groups, rheology and stability.

4.2 Materials and Methods

The AD sludge samples were collected from the Beenyup Wastewater Treatment Plant (WWTP) in Perth and were analysed immediately upon receiving. Sodium alginate, cellulose, yeast, potassium chloride (KCl) and calcium chloride ($CaCl_2$) were purchased from Sigma-Aldrich and used in the synthetic sludge formulation according to Dursun (2007) as described in Section 3.1.2. Type of cellulose and the ratio of KCl to $CaCl_2$ were examined in order to simulate the desirable properties of AD sludge in this study. The characteristics of the sludge sample were determined according to Standard Methods 2540 (APHA 2012) for the total solids (TS), total dissolved solids (TDS) and total suspended solids (TSS); Standard Methods 2710F for the specific gravity (SG) as well as the Reactor Digestion Method (Hach Method 8000, adapted from Standard Methods 5220D) for Chemical Oxygen Demand (COD) test.

4.3 Results and Discussion

4.3.1 Sludge characteristics

The AD sludge was dark brown in colour and gave off muddy odour. It flowed readily and settled when left undisturbed. The characteristics of the AD sludge were presented in Table 4.1, together with those of other sludge samples for comparison. It can be seen that most of the physical and chemical properties of the AD sludge applied in this work were comparable with the ones reported by Thapa et al. (2009) except for the mean particle size and zeta potential (ZP) value. The mean particle size of sludge samples in this work fell within the range of 80–100 μm and the ZP values were between –12 and –14 mV where both were of higher values than the literature data. The more positive ZP value corresponded to the bigger particle size with reduced surface-to-volume ratio and hence reduced negative surface charges for the AD sludge used in this study.

Table 4.1 Characteristics of sludge

Property	Anaerobically digested sludge	Modified synthetic sludge
Total solids (TS), g/L	14–16	15–16
Total dissolved solids (TDS), g/L	2–3	3–5
Total suspended solids (TSS), g/L	12–13	11–12
Specific gravity (SG)	1.000–1.005	0.984–0.986
Chemical oxygen demand (COD), g/L	15.9[a]	1.550
Capillary suction time (CST), s	140–160	120–160
pH	6.9–7.1	4.3–4.6
Electrical conductivity (EC), mS/cm	5.6–5.7	6.5–6.7
Mean particle size, μm	80–100	70–90
Zeta potential (ZP), –mV	12–14	14–16
Specific resistance to filtration (SRF), m/kg	n/a[b]	$2.2–2.6 \times 10^{14}$

[a] Reading taken from Yeneneh et al. (2013) who used the same digested sludge sample
[b] n/a stands for "not available"

As for the synthetic sludge, the properties were mostly analogous in comparison with those of the AD sludge, except for a few. The chemical oxygen demand (COD) value of the AD sludge was about an order higher than the one of synthetic sludge. This indicates that there are more organics in the real AD sludge with higher oxygen demand for breakdown. The synthetic sludge was also more acidic due to the presence of alginic acid but this could be adjusted by addition of alkaline (see Section 5.3.3). Besides, the synthetic sludge was found lighter with higher electrical conductivity due to the use of potassium salt in the formulation. The initial concern of using Dursun's formulation in synthetic sludge formulation was that the capillary suction time (CST) of the sludge prepared was too high (i.e. 560–580 s before modification) compared to the CST of the AD sludge. The CST values indicate the filterability or dewaterability of sludge. The small CST value indicates that the sludge is easy to dewater. This test was used as the primary dewaterability parameter for the rest of this study. Therefore modification of synthetic sludge was performed to bring the dewaterability characteristic closer to the one of AD sludge as shown in Table 4.1. This is extensively discussed in the following sections.

4.3.2 Modification of synthetic sludge

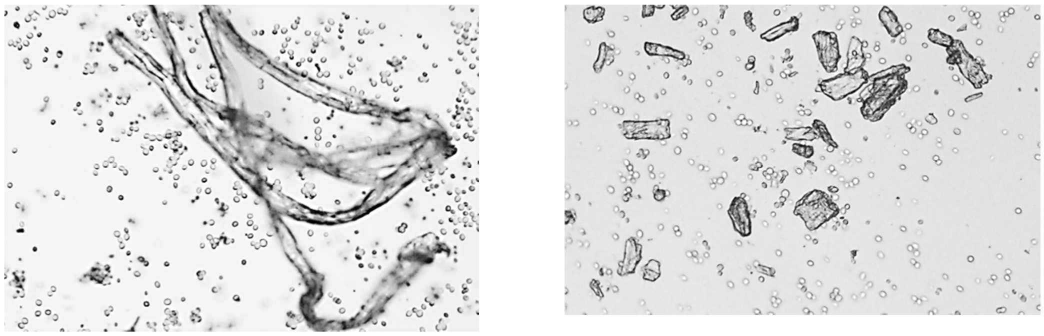
For the purpose of comparison and reproducibility, Dursun (2007) studied and developed a revised synthetic sludge formulation based on the previous work of Sanin and Vesilind (1996), Örmeci and Vesilind (2000) and Muller (2003) (unpublished, quoted in Dursun et al. (2004)). He proposed that the presence of alginate, potassium K^+ and calcium Ca^{2+} ions constitutes a gel (polymeric) fraction, whereas cellulose and yeast make up a particulate (structural) fraction in synthetic sludge slurry. Preliminary studies were carried out to determine the desired change in Dursun's formulation in order to simulate the properties of AD sludge as listed in Table 4.1.

(a) Effect of type of cellulose

The initial modification followed the suggestion of Örmeci and Vesilind (2000) to use medium fibrous cellulose to replace microcrystalline cellulose because of its size and shape resemblance to the filamentous bacteria. The change was applied to the synthetic sludge formulation from Dursun (2007). The composition of synthetic sludge remained unchanged for this study unless stated.

Particle size and shape

The modified synthetic sludge prepared with fibrous cellulose was examined and compared with the original formulation with microcrystalline cellulose using a Nikon Eclipse 50i microscope under 40, 100 and 400× magnifications. As shown in Figure 4.1(a), the fibrous cellulose exhibits long rod, tube shape ranges 90–360 μm in length and 10–20 μm in diameter (categorised as medium particle size from Sigma-Aldrich.com). Meanwhile the microcrystalline cellulose exhibits short rod shape and ranges 40–60 μm in length and 10–20 μm in diameter (Figure 4.1(b)). The mean particle size in length falls within the range of the one reported by Örmeci and Vesilind (2000) of 50–350 μm for medium fibrous cellulose and 25–75 μm for microcrystalline cellulose. Apart from cellulose, the tiny spherical structures observed in Figure 4.1 in both preparations are the yeast particles with the average size of 2.5–7.5 μm (further examined under 400× magnifications). This is close to the average particle size for individual bacteria in the biosolids structure (Li and Ganczarczyk 1990).

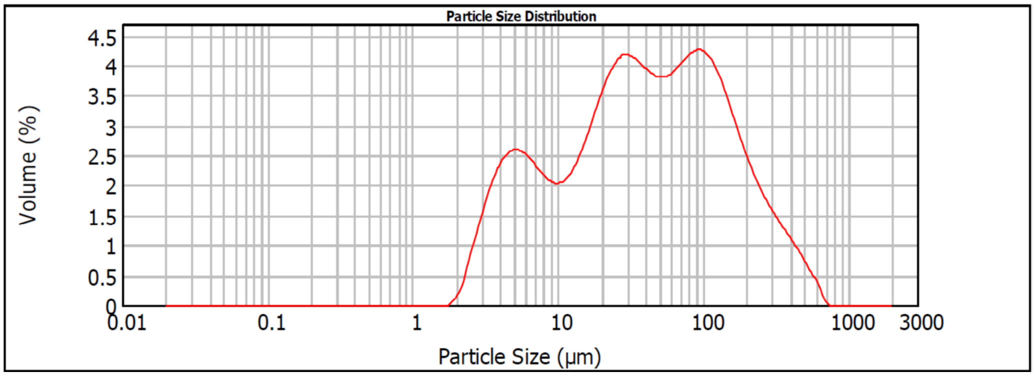


(a) (b)

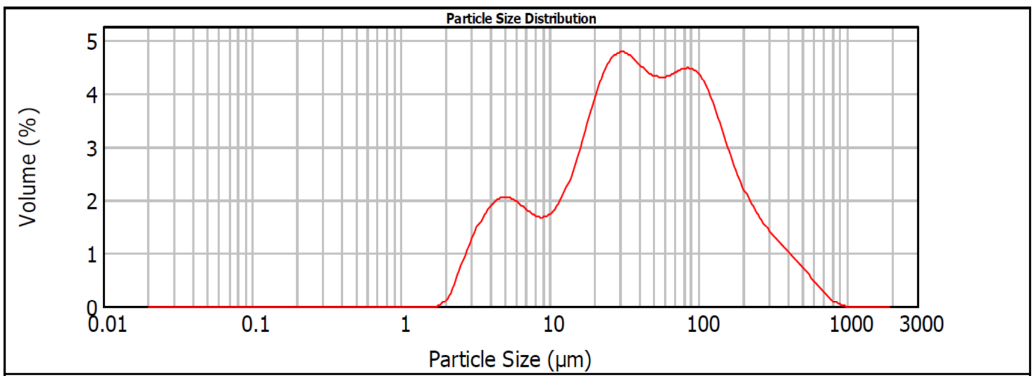
Figure 4.1 Micrographs of synthetic sludge prepared with (a) fibrous cellulose, and (b) microcrystalline cellulose (under 100× magnifications)

Particle size distribution

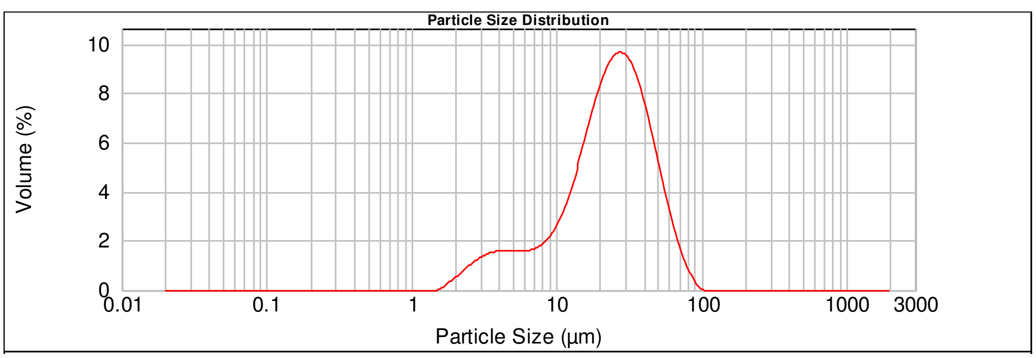
The particle size distributions of the synthetic sludge and AD sludge were illustrated in Figure 4.2. The volume weighted mean values of synthetic sludge prepared with fibrous cellulose were reported as 79 μm and 81 μm at pHs 4 and 7 respectively measured by the Mastersizer 2000 (see Figures 4.2(a) and (b)). The first peak depicts the particle size range of yeast while the second and third peaks refer to the broader range of fibrous cellulose found in the modified synthetic sludge system. It can be concluded from the data that the particulate fraction in the synthetic sludge comprises about 20% of yeast and 80% of fibrous cellulose in a volume proportion. Meanwhile the synthetic sludge prepared with microcrystalline cellulose showed a much lower particle size mean of 26 μm as given in Figure 4.2(c), which is consistent with the microscopic observation. The AD sludge however exhibited a more uniform particle size distribution with only one broad peak appearing near 100 μm (see Figure 4.2(d)).



(a) Synthetic sludge with fibrous cellulose at pH 4 (mean size 79 µm)

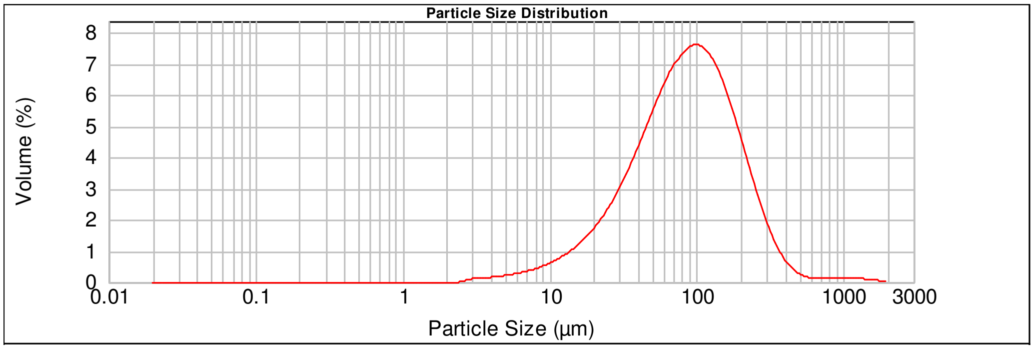


(b) Synthetic sludge with fibrous cellulose at pH 7 (mean size 81 µm)



(c) Synthetic sludge with microcrystalline cellulose (mean size 26 µm)

Figure 4.2 Particle size distribution of sludge



(d) AD sludge (mean size 100 µm)

Figure 4.2 Particle size distribution of sludge (continued)

Flocculation and dewatering behaviour

When conditioned with low molecular weight chitosan at the dosage of 15 g/kg, Figure 4.3 shows that both synthetic sludge systems prepared using different types of cellulose showed good dewaterability with the CST values reduced to 35.6 s and 11.4 s for microcrystalline cellulose and fibrous cellulose respectively. The presence of the filamentous backbone from the addition of fibrous cellulose gave better dewaterability to the sludge system. Örmeci and Vesilind (2000) also attributed the improvement in the dewaterability of synthetic sludge to the addition of fibrous cellulose which helped the formation of strong flocs by forming the rigid backbone. They observed good settling and compaction of the synthetic sludge due to the addition of right amount of fibrous cellulose. The sludge flocs formed with the two types of cellulose applied in this study were illustrated in Figure 4.4.

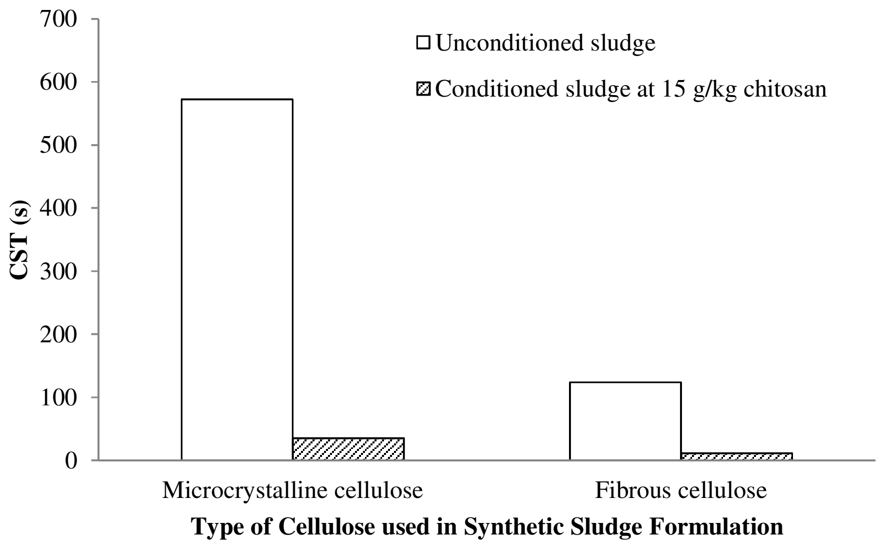


Figure 4.3 Comparison in sludge dewaterability as measured by CST using different types of cellulose in synthetic sludge formulation

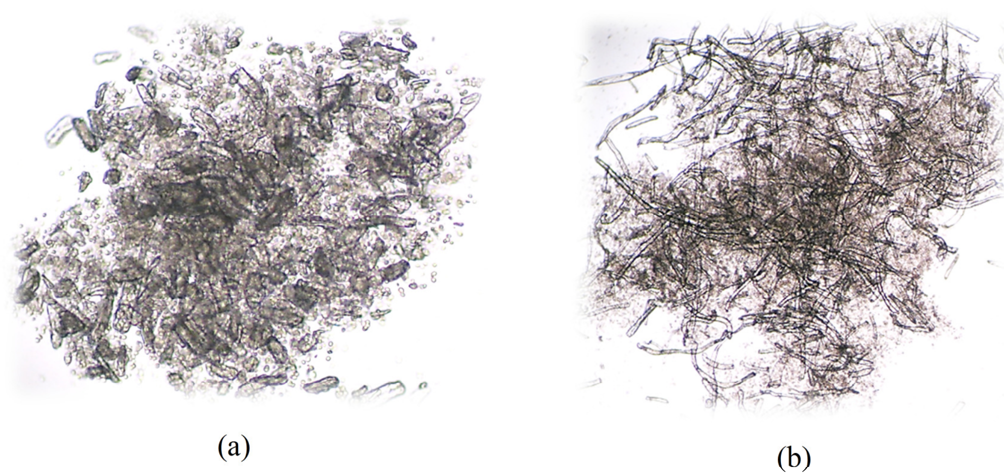


Figure 4.4 Floc structure formed from conditioned sludge prepared with (a) microcrystalline cellulose, and (b) fibrous cellulose (under 100× magnifications)

(b) Role and effect of each component in sludge formulation

To understand the role and effect of each component in sludge formulation on sludge dewaterability, the change in CST with sequential addition of each component in the preparation of the modified synthetic sludge with fibrous cellulose as outlined in Section 3.1.1 was studied. As shown in Figure 4.5, the initial alginate solution was viscous with a CST value of 124.0 s (Step 1). Addition of cellulose and yeast into alginate in Step 2 raised the CST to 211.9 s due to the ionisation and interactions of functional groups among the components. With the subsequent addition of K^+ and Ca^{2+} ions (Steps 3 and 4), increased interactions between alginate, cellulose and yeast caused a significant rise in CST to 703.3. After washing and dilution, the CST dropped to 135.8 s. Modification of pH from 4 to 7 did not significantly change the CST value (from Step 6 to Step 7). No significant change in mean particle size with respect to this change of pH was also observed in the previous section (see Figure 4.5).

In this work, alginate was used to simulate the extracellular polymeric substances (EPS) present in sludge, and Ca^{2+} ions were used as the bridging cations. It is well known that alginate aggregation is specific for Ca^{2+} and that the concentration of Ca^{2+} affects the settling and dewatering properties of sludge (Sobeck and Higgins 2002). Ca^{2+} ions are crucial in forming a gel fraction with alginate and promoting binding between cellulose, yeast and alginate (Dursun and Dentel 2007). Cations enhanced the attachment of alginate onto the surface of cellulose and yeast particles by reducing the electrical double layer (Dursun 2007). Cellulose and yeast served as the filamentous backbone and bacteria forming the particulate fraction of the sludge.

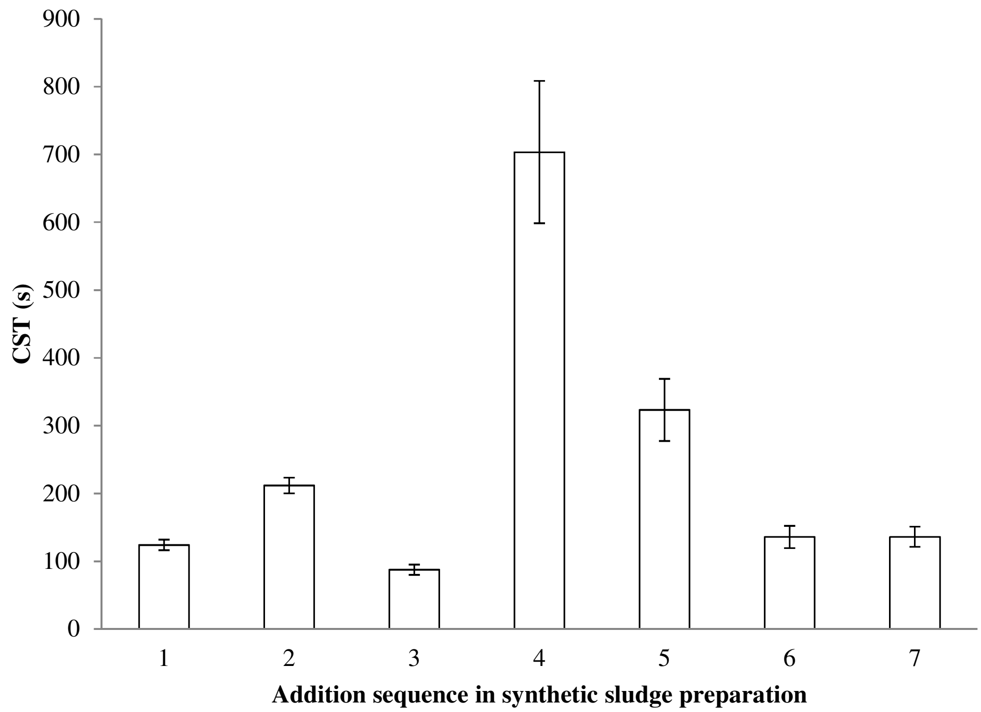


Figure 4.5 Change in CST with sequential addition of each component in synthetic sludge preparation (1: alginate; 2: cellulose and yeast; 3: potassium; 4: calcium; 5: washing and settling; 6: dilution; 7: pH modification)

(c) Effect of monovalent to divalent ratio of cations

Higgins and Novak (1997) proposed that the monovalent to divalent (M/D) ratio is significant in determining the floc properties. The following studies therefore examined the change in M/D ratio of K^+ to Ca^{2+} ions (expressed in milliequivalents as meq/meq) in order to bring the CST closer to the one of digested sludge. Results in Table 4.2 reveal that increasing M/D ratio (reducing Ca^{2+} ion concentration) leads to reducing CST (higher dewaterability). From visual observation, gel fraction formed in sludge after overnight settling decreased from 84.2% to 21.1% with increasing M/D ratio from 9.1 to 18.2. At M/D ratio of 18.2, the sludge exhibited mainly a particulate form of sludge rather than gel. This is undesirable as there is lack of binding between cellulose, yeast and alginate which makes solid/liquid separation occur readily. Therefore the original M/D ratio of 9.1 in Dursun's formulation was adopted for the remaining studies with desired dewaterability characteristic. On the other hand, it is interesting to note that in the absence of K^+ ions when M/D ratio was 0, addition of Ca^{2+} ion in sludge preparation formed flocs which gave a very low CST value of 14.4 s. As mentioned in Section 4.3.2(b), the presence of divalent cations, Ca^{2+} ions in this case, is believed to act as a bridge between the negatively charged sites within the synthetic sludge to aid the flocculation process (Higgins and Novak 1997, Sobeck and Higgins 2002). Therefore addition of Ca^{2+} ion alone can greatly improve the settling and dewatering behaviour of sludge, leading to low CST when M/D ratio was 0.

Table 4.2 Effect of monovalent to divalent (M/D) ratio of cations on CST

M/D ratio	CST (s)
0.0[a]	14.4
9.1	152.9
12.1	118.7
18.2	62.5

[a] With respect to 2 meq of Ca^{2+} (in the absence of K^+)

(d) Morphology and infrared spectra analysis of modified synthetic sludge

The morphology of the modified synthetic sludge was observed under the scanning electron microscope (SEM) under 100× magnifications in order to examine the shape, texture and distribution of materials at the sludge surface, as shown in Figure 4.6. Fibrous structures of about 100–300 μm were observed to intermingle and stack on each other. Tiny yeast particles (representing microorganisms) scattered around the fibrous structures with a number of them attached to the surface of the fibres. This image visualises the collection of yeast particles as bacterial colonies captured within a structure held together with filamentous organisms as described by Vesilind (1994).

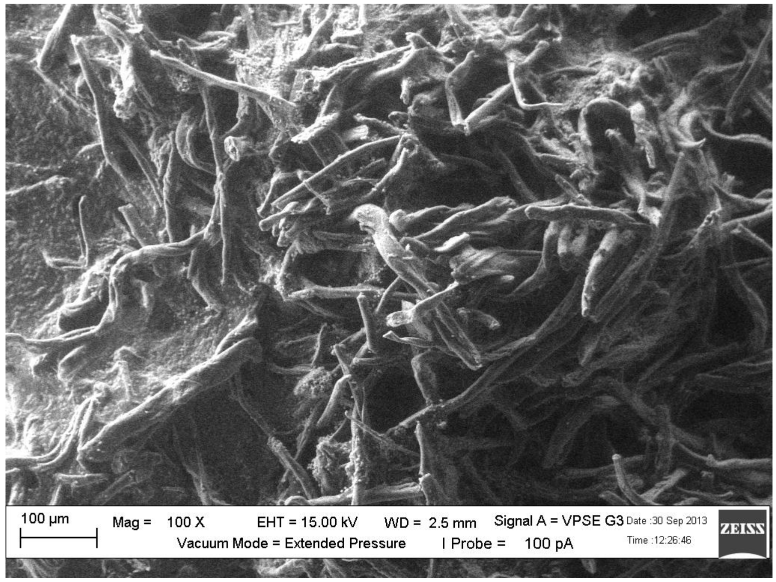


Figure 4.6 SEM image of synthetic sludge prepared with fibrous cellulose

In order to examine the organic chemical groups and the interaction of each component in the synthetic sludge, the Fourier Transform Infrared (FTIR) spectra of the sludge together with the individual organic components used in the formulation were analysed and presented in Figure 4.7. A strong infrared absorption band is found at 3280–3340 cm^{-1} for all spectra, corresponding to the O–H stretching vibration of alcohols and carboxylic acids (Rubinson and Rubinson 2000), which present in the two polysaccharides (alginate and cellulose) and yeast used in the formulation as shown in Figure 4.7. For the yeast's spectrum, the two bands at 2852 and 2921 cm^{-1} are asymmetric and symmetric vibration of CH_2 of lipids and aliphatic structures in yeast cells, respectively. These values are similar to the ones of activated sludge reported by Guan et al. (2012). Meanwhile the band at 2901 cm^{-1} can be attributed to the CH_2 stretching in cellulose as well. The band around 1630–1645 cm^{-1} can be assigned to the C=O stretching to a different extent for each spectra. Due to the complex structure of yeast as a microorganism compared to the other organic compounds, the bands at 1641 cm^{-1} and 1539 cm^{-1} for yeast are more intense due to the possible presence of C=N stretching, C=C stretching or N–H bending in the cells.

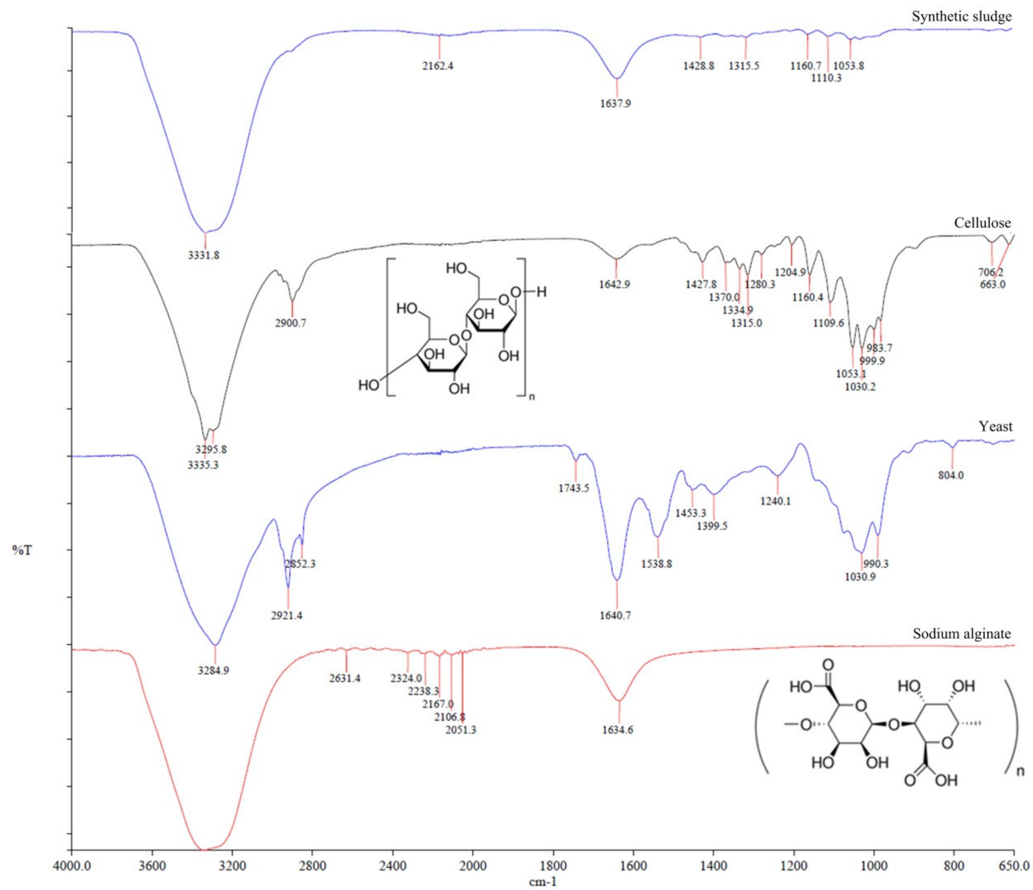


Figure 4.7 FTIR spectra of synthetic sludge and its respective organic components

Rubinson and Rubinson (2000) pointed out that the region between 910 and 1300 cm^{-1} is generally used as a "fingerprint" for organic compounds as the peaks within the region are most sensitive to differences in compound structure. The distinct set of bands observed between 800 and 1455 cm^{-1}, especially for cellulose and yeast, in the present study closely matches the proposed fingerprint region for identification of these components. These intense and characteristic bands diminish when alginate molecules attach to cellulose and yeast in aqueous phase during mixing to make up the synthetic sludge.

4.3.3 Rheological properties of modified synthetic sludge

Figure 4.8 presents the results of repeated rheological measurements on the modified synthetic sludge suspension with total solids of 15–16 g/L at 25°C. The rheograms indicate that the synthetic sludge exhibited a non-Newtonian behaviour which followed the power-law model, also known as the Ostwald-de Waele model, $\tau = K\dot{\gamma}^m$ (where τ is the shear stress in Pa, $\dot{\gamma}$ the shear rate in s^{-1}, *K* the consistency index in Pa.s^m and *m* the power-law or the flow behaviour index, dimensionless) (Peker and Helvaci 2008). The best fit results for the data were found at the average *K* value of 0.0289 and *m* of 0.5775. The correlation coefficient of R^2 with the average value of 0.9335 indicated a satisfactory fit using this model. There was no significant yield stress τ_0 found in the sludge rheogram.

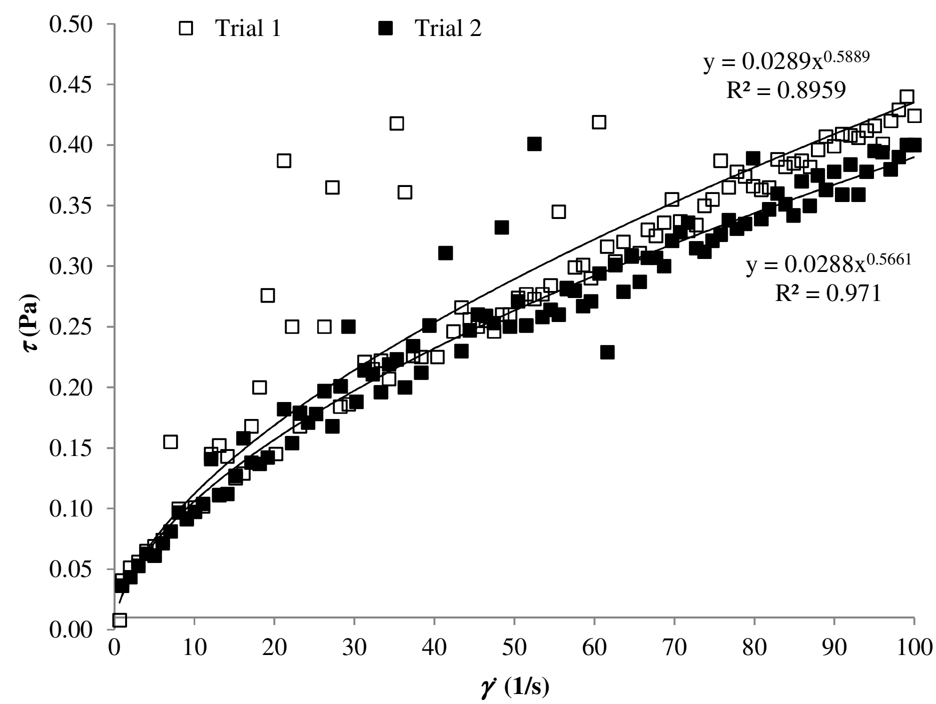


Figure 4.8 Rheogram of modified synthetic sludge with total solids of 15–16 g/L

The results from this study are in agreement with the findings of Wang and Dentel (2011). They studied the rheological properties of AD sludge and found that it followed the power-law model with the *K* values of 0.8948–1.144 and *m* of 0.3479–0.3507 for the sludge with total solids of approximately 28–31 g/L. The lower *K* value and higher *m* value due to the lower sludge concentration in this study indicate that the dilute sludge experiences less shear stress as compared to the concentrated sludge, and is approaching Newtonian behaviour if it is diluted further.

As shown in Figure 4.9, this type of fluid with a power-law index of $m < 1$ modelled a shear-thinning behaviour where the material apparent viscosity decreased when the shear rate was increased. It is also known as a pseudoplastic fluid (Peker and Helvaci 2008). The apparent viscosity approaches a near-constant value of about 4.00–4.25 mPa.s at the shear rate of 100 s^{-1} (compared to the viscosity of water which is 0.890 mPa.s at 25°C).

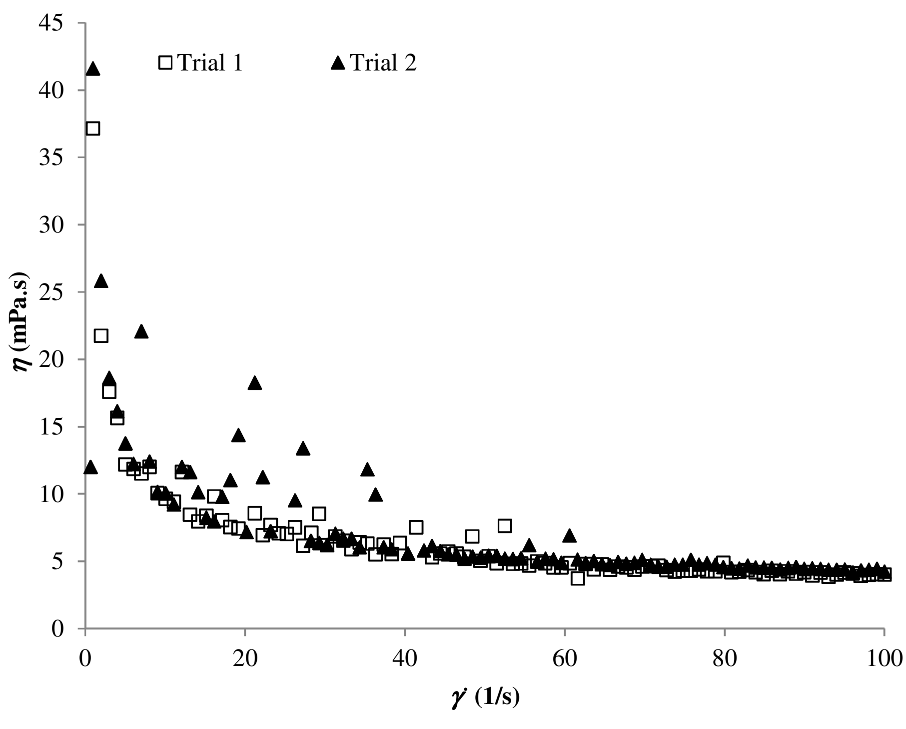


Figure 4.9 Change in apparent viscosity with increasing shear rate for modified synthetic sludge with total solids of 15–16 g/L

4.3.4 Stability of modified synthetic sludge

In order to examine the stability of the modified synthetic sludge, the change in CST was observed over a period of 32 days where the sludge was stored at 4°C when not in use. Figure 4.10 shows that the CST values fluctuated significantly between Day 10 and Day 20. The pH values however did not change much and recorded an average of about 4.6–4.7. The storage period had a substantial effect on sludge dewaterability. Intriguingly, the CST returned to the initial value at the end of Day 32. The results suggest that the sludge may be stored for an extended period to fully stabilise it before usage. Similar statement was made by Baudez and co-workers (2011) where they stored the AD sludge samples at 4°C for 30 days before experiments, in order to reduce temporal variability. The researchers believed that the potential for organic changes in sludge was reduced by storing the sludge sample for such an extended period.

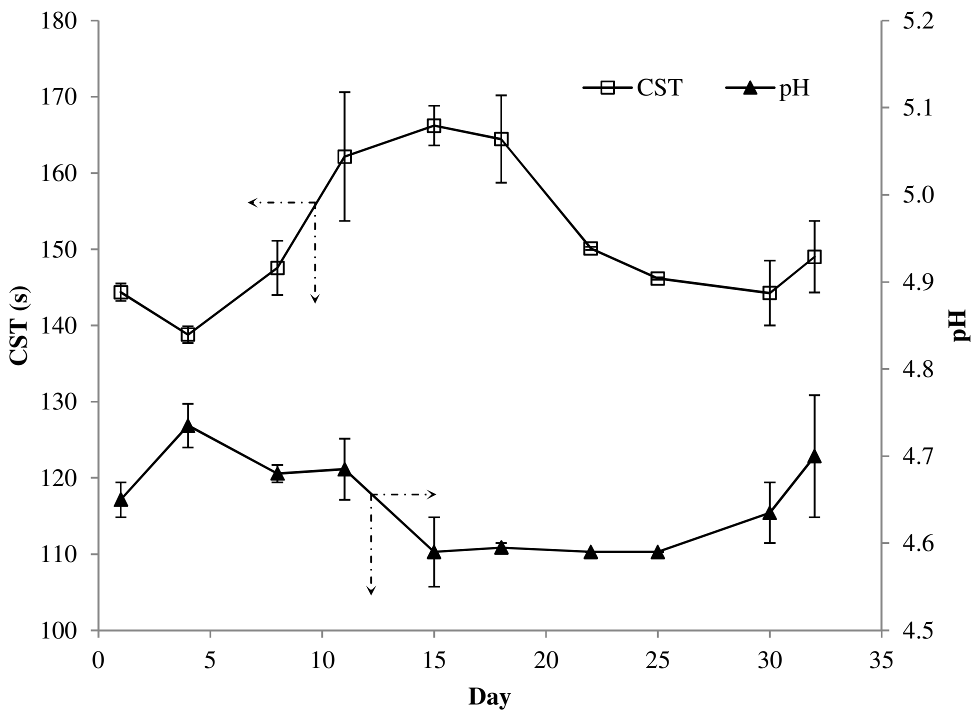


Figure 4.10 Change in CST and pH with days of storage

4.4 Conclusion

The characteristics of AD sludge and synthetic sludge were analysed in this chapter. Based on the study on the type of cellulose, addition sequence and monovalent to divalent ratio of cations, the synthetic sludge formulation was modified to replace microcrystalline cellulose with fibrous cellulose so as to bring the dewaterability characteristic closer to the one of digested sludge. Examination of the sludge morphology, infrared spectra and rheological properties suggested that the modified sludge has high degree of similarity to the AD sludge. In addition, it was found that the sludge may be stored for a period of 32 days to fully stabilise it. In conclusion, the modified synthetic sludge is deemed sufficient to simulate some relevant physical and chemical properties of AD sludge such as the solids content, dewaterability (or filterability), particle size, pH and zeta potential value for the following study of conditioning and dewatering.

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CHAPTER 5

DEWATERABILITY STUDIES OF SLUDGE CONDITIONING UNDER VARIOUS PHYSICOCHEMICAL PROCESS PARAMETERS*

5.1 Introduction

Various physicochemical process parameters are known to affect the operational performance of sludge dewatering in terms of dewatered cake solids content, filtrate quality and chemical consumption. The effectiveness and required dosage of conditioning chemicals are often evaluated by use of a jar test apparatus in a typical treatment plant. This work used a series of 250-mL beakers to simulate a mixing, flocculation, and settling cycle as in a jar test apparatus. The effects of molecular weight and dosage of polymer are first presented and discussed using various dewaterability measurement parameters to gauge the performance. The role of various cationic polymers and inorganic conditioning materials on anaerobically digested (AD) sludge and synthetic sludge has been tested in this study. The results of jar testing under various process conditions such as pH, temperature, mixing speed and mixing time on flocculation and dewaterability are discussed here.

5.2 Materials and Methods

Sludge samples and conditioning chemicals were prepared according to Section 3.1. A series of 250-mL beakers were set up similar to the jar test to conduct batch conditioning experiments in studying the effects of conditioner dosage and type, pH, temperature, mixing speed and mixing time on sludge dewatering performance. The desired amount of conditioner was gradually dosed into a 100-mL aliquot of sludge sample in the beaker within 30–60 s to ensure uniform dispersion. The conditioned

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* Part of this chapter has been presented in *Chemeca 2014*, Perth. A manuscript is under preparation for submission to journal.

sludge was then rapidly stirred at 300 rpm for 60 s to aid the coagulation and subsequently stirred at 50 rpm for 300 s to promote flocculation. These mixing conditions were used in all experiments except for the study of the effects of mixing speed and mixing time during the flocculation step (slow mixing). The dewatering performance of the conditioned sludge was assessed at the end of mixing using various measurements such as capillary suction time, turbidity, electrical conductivity, zeta potential, cake solids content, particle size, Fourier Transform Infrared spectrum and microscopic imaging.

5.3 Results and Discussion

5.3.1 Effects of molecular weight and dosage of polymer on sludge flocculation and dewatering

(a) Effect of molecular weight on dewaterability

Figure 5.1 illustrates the effect of molecular weight (MW) and dosage of polymer on the capillary suction time (CST) for the conditioning of AD sludge. The CST test was used as the primary dewaterability parameter to characterise the sludge dewatering performance. With increasing polymer dosage, the CST decreased rapidly and eventually reached a plateau for both the low MW and medium MW chitosans. Medium MW chitosan reduced the CST further by 27% compared to the low MW chitosan at plateau. The commercial high MW polymer, EMA 8845 showed a gradual decrease in the CST in response to increasing polymer dosage and reached a similar CST value as the medium MW at 19 g/kg. Overdosing EMA 8845 led to super-flocculation causing the CST readings less meaningful as it was possible to pour only liquor in the CST funnel, rather than sludge solids.

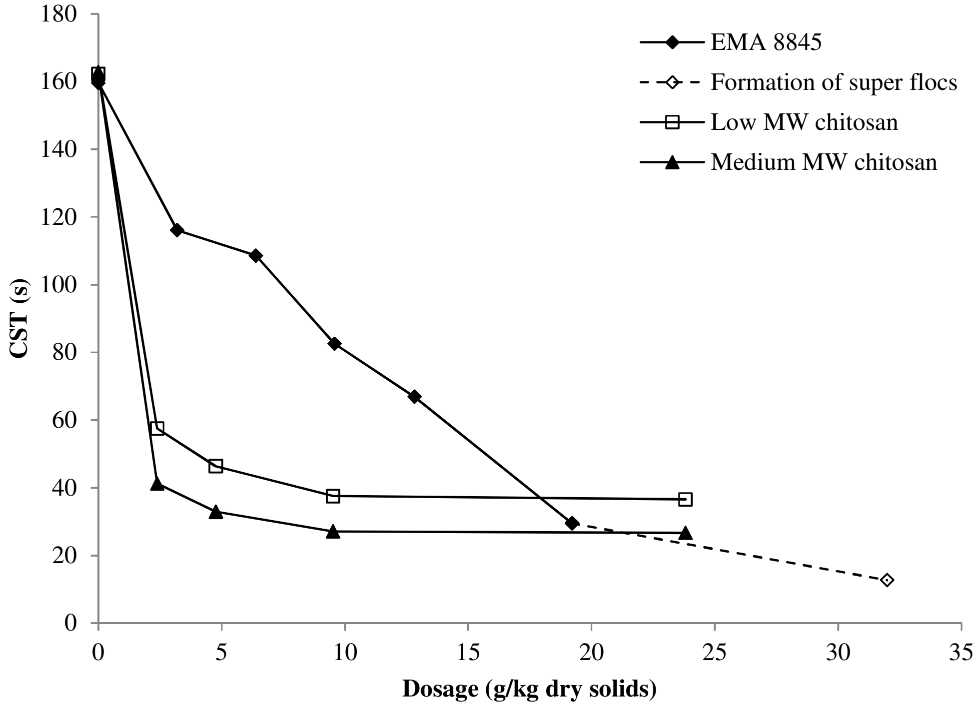
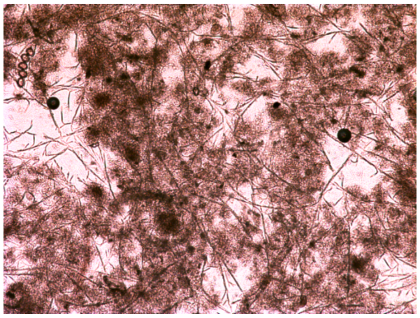


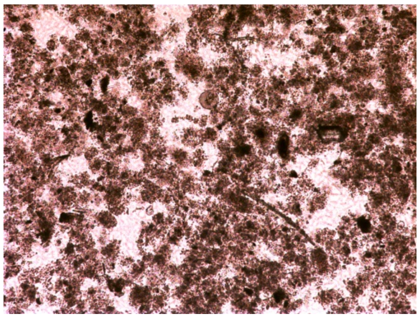
Figure 5.1 Effect of molecular weight and dosage of polymer on sludge dewaterability measured by CST

The MW of a polymer has a significant effect on sludge conditioning. It is well known that increase in MW of a polymer may allow its cationic sites to bind to more particles, thus bridging the solid particles in the suspension system (Dentel 2010). This will result in the formation of larger flocs which may be separated easily from the treated suspension. Sanin et al. (2011), however, pointed out that the longer polymer chains may tend to adsorb only on the outside of the sludge flocs where they inhibit more polymers from entering the flocs. More intrafloc waters are then trapped causing wetted sludge cake with increased moisture content. This is in line with the observation in this study where large and fluffy flocs were formed by EMA 8845 especially at higher dosage and significant amount of water was trapped in the flocs. On the other hand, low to medium MW chitosans were found effective at even very low dosages. It is proposed that the shorter polymer molecules may diffuse more readily to bind the sludge particles where they can penetrate into the flocs, neutralise the charges and aggregate (Sanin et al. 2011). Increasing polymer dosage yields no further improvement in sludge dewaterability, as shown in Figure 5.1, probably due to the lack of unoccupied sludge surfaces for further adsorption.

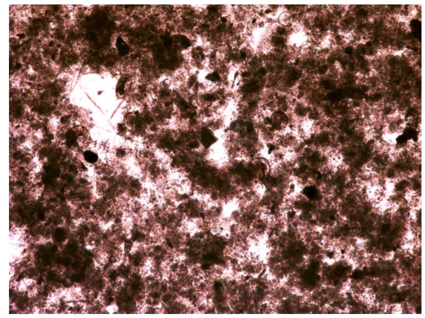
Figure 5.2 shows the formation of flocs observed under light microscope after AD sludge was conditioned with low MW and medium MW chitosans respectively at different dosages. The floc image of unconditioned AD sludge is given in Figure 5.2(a) for comparison. The vacant sites indicate the water captured in the interstitial spaces within flocs and within cells as interstitial water in AD sludge, as described earlier in Section 2.4. It is obvious that small and discrete sludge flocs were formed after conditioning with low MW chitosan as shown in Figure 5.2(b) while longer chains of flocs seemed to form after conditioning with medium MW chitosan at the same dosage of 5 g/kg as shown in Figure 5.2(e). The flocs grew bigger and became more compact with more free water released at increasing dosages as observed from Figures 5.2(b)–(d) for low MW chitosan and Figures 5.2(e)–(g) for medium MW chitosan. These images imply the positive effect of increasing chitosan dosage in promoting the flocculation of sludge.



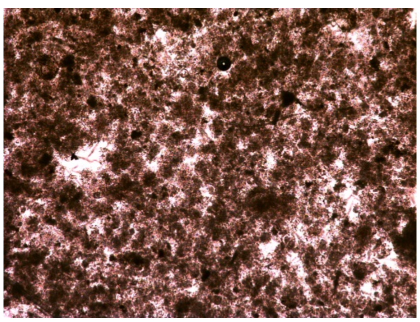
(a) Unconditioned AD sludge



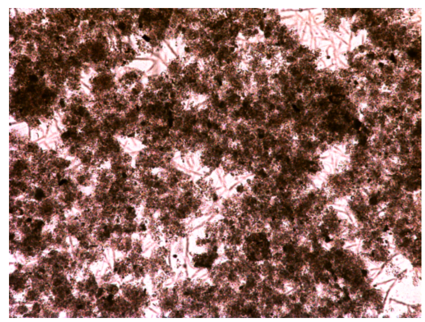
(b) 5 g/kg low MW chitosan



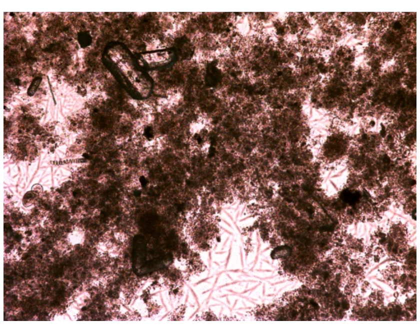
(e) 5 g/kg medium MW chitosan



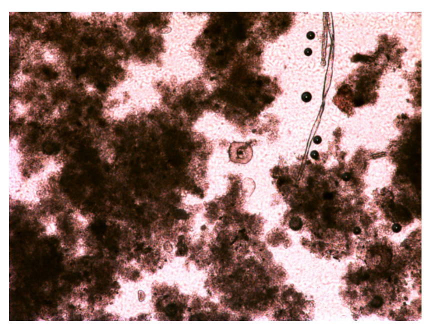
(c) 10 g/kg low MW chitosan



(f) 10 g/kg medium MW chitosan



(d) 25 g/kg low MW chitosan



(g) 25 g/kg medium MW chitosan

Figure 5.2 Formation of sludge flocs when conditioned with different MW chitosans

(b) Effect of conditioning dosage on dewaterability using low MW chitosan

In the following study, low MW chitosan was applied in both AD sludge and synthetic sludge systems to further examine the effect of dosage on sludge dewaterability. As shown in Figure 5.3, as the dosage increased, the CST decreased rapidly and eventually reached a plateau after 10 g/kg and 20 g/kg respectively for AD sludge and synthetic sludge. The inset in Figure 5.3 shows the inverse of CST value which is indicative of the rate of water release from sludge. The results suggest that addition of chitosan increased the rate of water removal from AD sludge at low dosage but after 10 g/kg, the rate remained constant and the minimum CST achieved was only 36.6 s. Meanwhile the rate of water release from synthetic sludge was lower at low dosage but increased gradually to 0.15 s^{-1} at 20 g/kg with the lowest CST achieved at 6.6 s which was close to the one of distilled water.

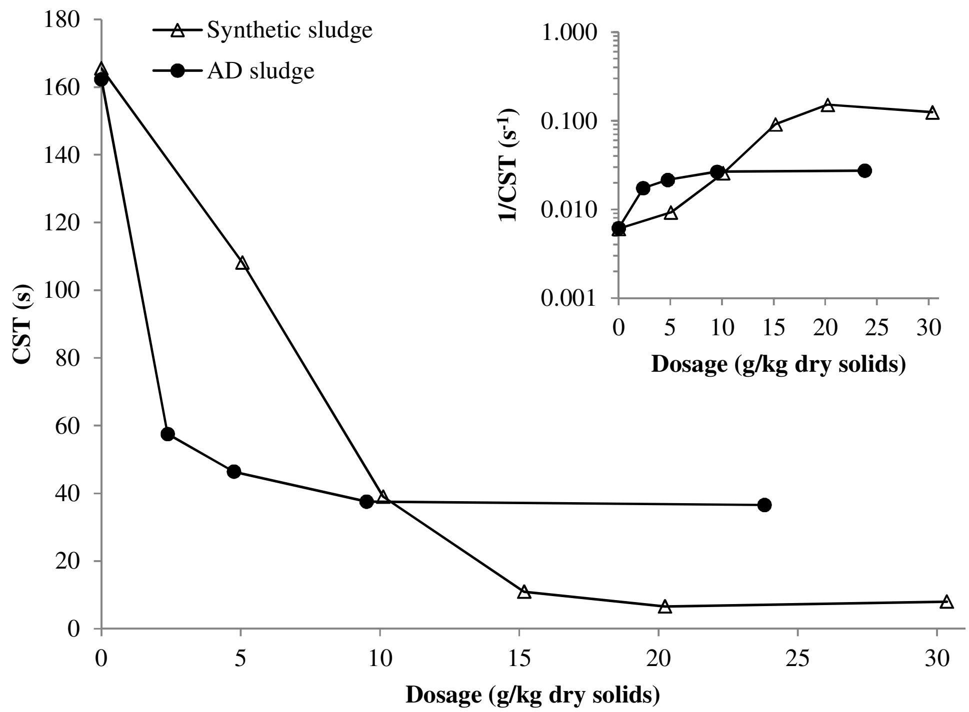


Figure 5.3 Effect of chitosan dosage on CST in conditioning of AD sludge and synthetic sludge (the inset represents the inverse of CST)

Figures 5.4 and 5.5 depict the formation of sludge flocs at low and high chitosan dosages in the two sludge systems. In comparison with the unconditioned AD sludge and synthetic sludge in Figures 5.4(a) and 5.5(a), small and discrete sludge flocs were formed when conditioned at low chitosan dosage (see Figures 5.4(b) and 5.5(b)) while big and lumpy sludge flocs were formed at high dosage (see Figures 5.4(c) and 5.5(c). After settling, clear supernatant was found at high dosage. Increase in floc size and supernatant clarity as a result of chemical dosing were discussed further in Section 5.3.1(c). Despite its lower MW, chitosan applied in this study was an effective conditioning aid in sludge flocculation and dewatering.

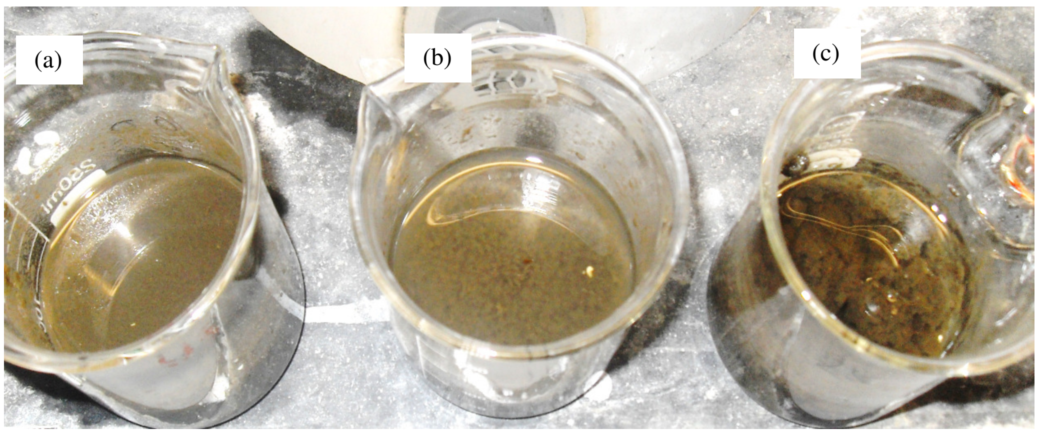


Figure 5.4 Flocs formed (a) before conditioning and after conditioning at (b) low dosage and (c) high dosage of chitosan in AD sludge

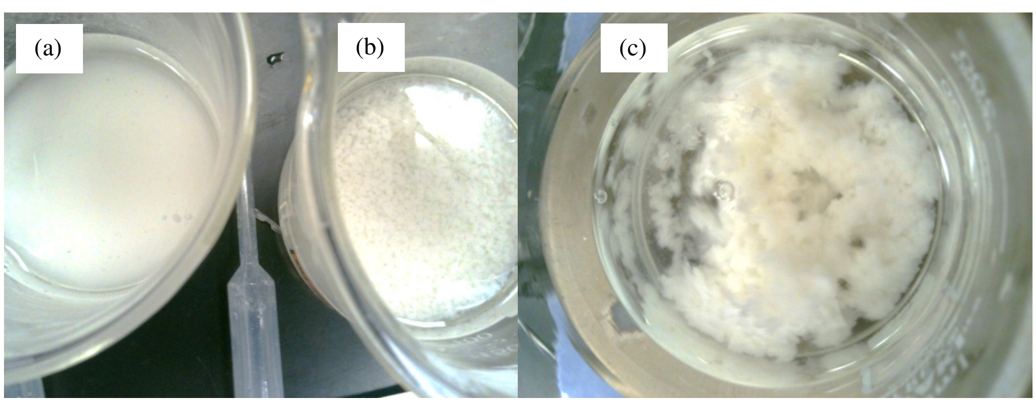
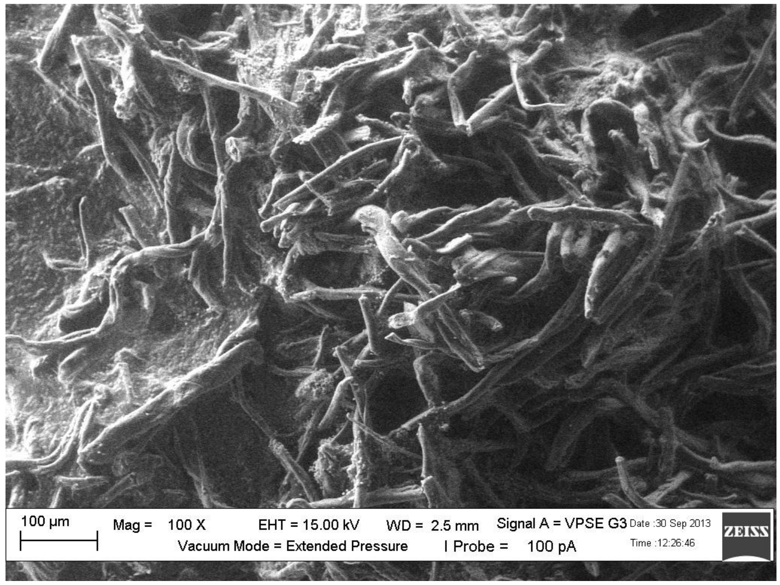


Figure 5.5 Flocs formed (a) before conditioning and after conditioning at (b) low dosage and (c) high dosage of chitosan in synthetic sludge

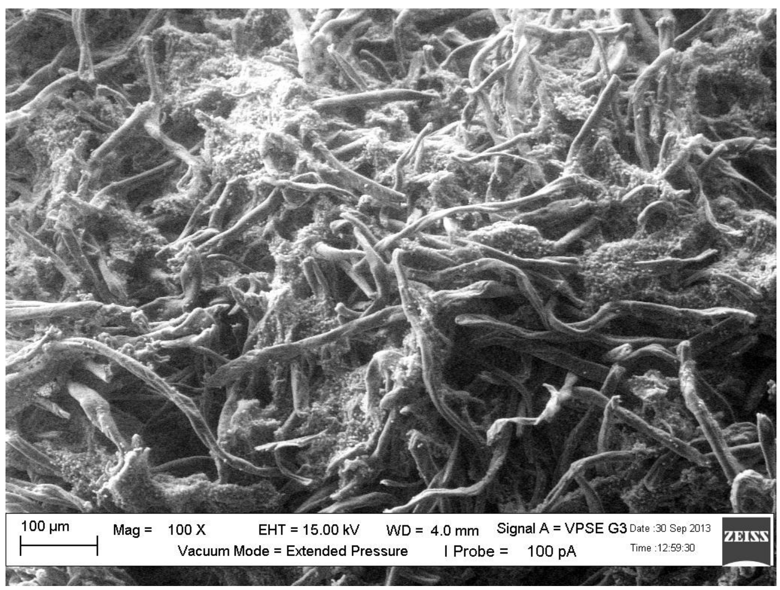
The sludge floc structure formed before and after chitosan conditioning in synthetic sludge was observed under the scanning electron microscope (SEM) under 100× magnifications as shown in Figure 5.6. The unconditioned sludge in Figure 5.6(a) shows loosely bound fibrous structures with tiny particles scattered around. There seems to be a great deal of interstitial or unoccupied spaces within the sludge flocs where water and various dissolved chemicals may form the continuum surrounding the flocs according to Vesilind (1994). When chitosan was introduced into the sludge system, Figure 5.6(b) depicts that the fibrous structures became more closely packed to each other with increased number of tiny particles attached to them. The electrostatic interactions between the cationic chitosan and the anionic sludge may allow more adsorption and charge neutralisation where the heterogeneous structures of sludge can be held together by strands of chitosan polymer, leading to agglomeration of sludge.

(c) Correlation of capillary suction time with other dewaterability parameters

To determine the optimum polymer dosage in sludge conditioning using low MW chitosan, the CST parameter was correlated to the measurements of supernatant turbidity, electrical conductivity (EC), zeta potential (ZP), filtered cake solids content and floc size using synthetic sludge as controlled experiments. Figure 5.7 shows the various dewaterability responses to the change in chitosan dosage. With increasing dosage, supernatant turbidity of the conditioned sludge after 30 minutes settling declined significantly with slight increase after 20 g/kg. Chitosan conditioning effectively removed the suspended sludge particles by the formation of flocs that settled and gave clear supernatant, as shown in Figure 5.5(c). The turbidity reduced by two orders with the lowest 35.4 NTU recorded at the dosage of 20 g/kg, consistent with the lowest CST value of 6.6 s obtained which indicated good dewaterability (see Figures 5.7(a) and (b)).



(a) Before conditioning



(b) After conditioning

Figure 5.6 SEM image of synthetic sludge before and after conditioning

Electrical conductivity (EC) has been claimed to be a good indicator for dewaterability by Sriwiriyarat et al. (2008). Figure 5.7(c) shows that the EC readings decreased gradually from 7.0 mS/cm to 6.5 mS/cm with increasing chitosan dosage. There was no clear indication of optimal dosage as measured by CST and turbidity. The decrease of EC may be attributed to the capture of the negatively charged sludge particles by agglomeration which reduced electrical mobility in the liquid medium. Addition of extra cationic chitosan up to 30 g/kg did not result in an increase in EC. The findings contradicted the work of Sriwiriyarat et al. (2008) where EC increased after reaching a minimum with increasing polymer dosage as a result of the residual cationic polymer. It is possible that the cationic polymer in their work has a relatively higher EC since the increase of EC after reaching the minimum point was higher than the one before conditioning. In the present study, the stock solution of chitosan polymer was found to have very low EC value of 1245 μS/cm. Therefore the residual cationic chitosan in sludge did not contribute significantly to the change of EC over the range of chitosan dosage applied.

The measurement of surface charge using ZP in function of the polymer dosage is often used to determine the polymer demand (Kopp and Dichtl 2001). The development of a net negative charge at the sludge surface is mainly due to the presence of the extracellular polymeric substances (EPS) which cause repulsion between the sludge particles (Chitikela and Dentel 1998, Mikkelsen and Keiding 2002). In this study, an optimum dosage may be identified when these electrostatic repulsive forces are counterbalanced and the value of the ZP in the supernatant approaches ±0 mV (causing destabilisation). It can be seen from Figure 5.7(d) that the magnitude of the ZP changed from –15 mV to 25 mV as the chitosan dosage increased from 0 g/kg to 30 g/kg. Increasing chitosan dosage increased the ZP till it reached a zero value near the dosage of 15 g/kg chitosan where very low CST and turbidity values were recorded at this dosage as well. Charge reversal occurred at 20 g/kg where the ZP value reached 21 mV but no significant change was observed for the CST and turbidity at this point. Further increase in dosage led to overdosing and the dewaterability results decreased as indicated by the increase of supernatant turbidity at 30 g/kg as a result of charge reversal and floc dispersal (Sanin et al. 2011).

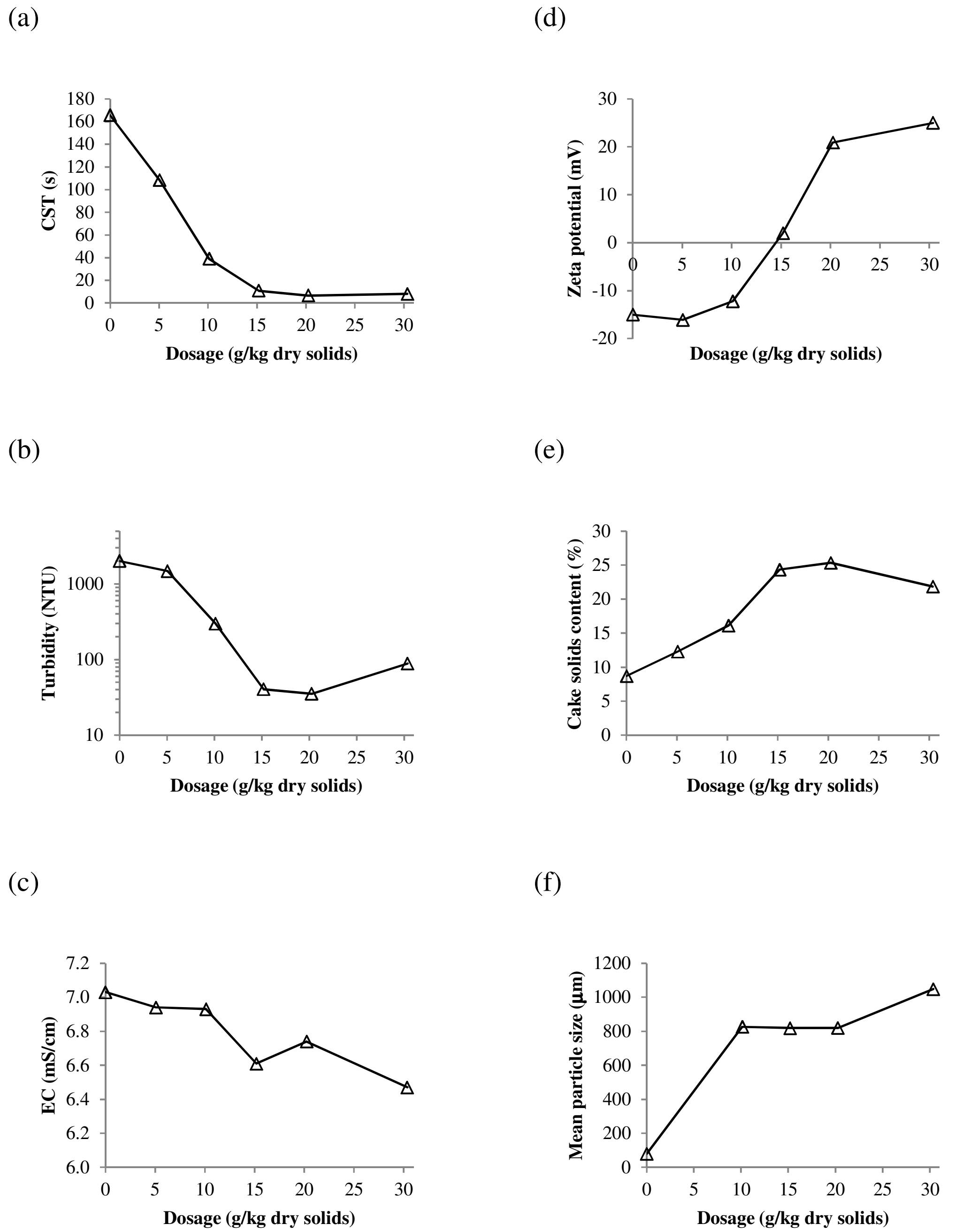


Figure 5.7 Responses of various sludge dewaterability measurements with respect to the change in chitosan dosage: (a) CST, (b) turbidity, (c) EC, (d) zeta potential, (e) cake solids content, and (f) mean particle size

It is also evident from Figure 5.7(e) that the cake solids content increased from 8.7% for the unconditioned sludge to the maximum of 25.3% at the dosage of 20 g/kg. The cake solids content reduced to 21.8% at 30 g/kg after passing the maximum point which may be attributed to the overflocculation phenomenon where more waters were trapped in the flocs. Looking at the largest mean floc size formed at 30 g/kg which was 1048 µm as shown in Figure 5.7(f), it is suggested that these bulky flocs actually contained lots of trapped water which did not correspond to the optimum dewaterability as the turbidity increased and the cake solids content reduced although low CST value was recorded. Meanwhile the floc size formed between 10 and 20 g/kg chitosan was found almost constant with the average value of 822±3 µm. The particle size distributions were also consistent for the flocs formed between 10 and 20 g/kg chitosan as shown in Figure 5.8.

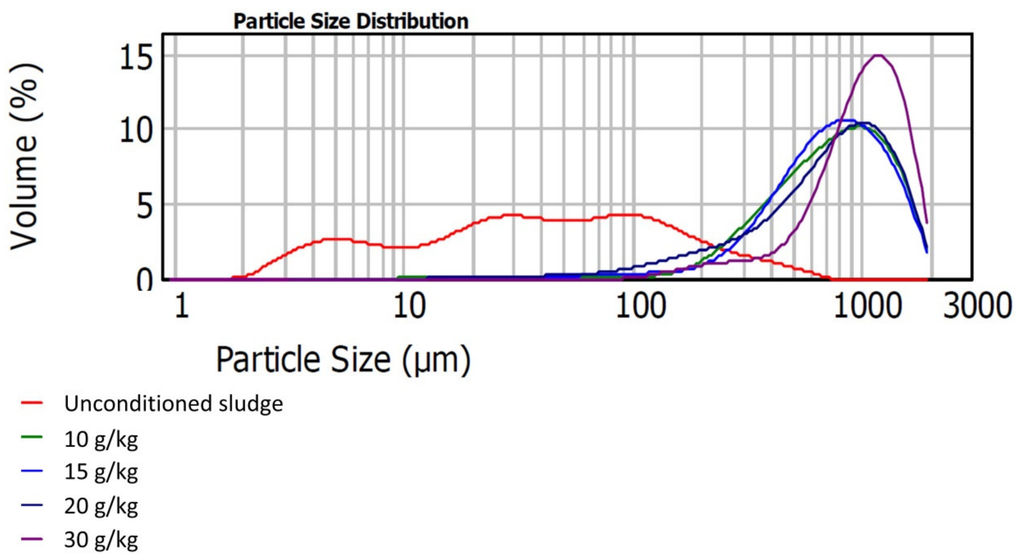


Figure 5.8 Particle size distributions with respect to the change in chitosan dosage

In consideration of the above sludge dewaterability parameters, it can be concluded that the optimum dosage of conditioner may be determined from the lowest CST and supernatant turbidity values, and the highest dewatered sludge cake solids content. The results suggested that the range of 15–20 g/kg chitosan was the optimum chemical dosage for this study where the favourable values of CST, turbidity and cake solids content were attained between 6.6–11.0 s, 35.4–40.6 NTU and 24.3–25.3% respectively. On the other hand, seeing that charge reversal at 20 g/kg did not significantly affect the CST, turbidity and cake solids content, it is possible to justify that strong adsorption of polymer molecules onto the sludge particles occurred at this point, making the flocculation process irreversible in equilibrium. Hence effective conditioning still occurred at 20 g/kg though the ZP value was 21 mV. Several researchers also suggested that dosing to achieve charge neutralisation may not always give a reliable prediction of optimum dosage for good conditioning (Cole and Singer 1985, Kaseamchochoung et al. 2006). However ZP measurement provides important information about the conditioning mechanism where charge neutralisation takes place approaching the optimum dosage. The sludge floc size may also give a relative indication of the flocculation behaviour but it is not able to gauge the extent of sludge dewatering.

In practice, a simple jar test is frequently applied in wastewater treatment plants to evaluate chemical conditioning. This test however relies only on the clarity of the supernatant and the appearance of the floc structure as a quick qualitative indication of the choice of conditioner and its ability (Sanin et al. 2011). As found in this work, the supernatant clarity is indeed a practical method for screening of conditioner and dosage but it needs to be quantified by the measurement of turbidity. On the other hand, judging the appearance of the floc structure may be misleading as it does not consider the amount of trapped water which may affect the sludge solids content after dewatering. Therefore this study proposes that the effectiveness of chemical conditioning can be assessed meticulously using the four useful dewaterability parameters, i.e., CST, supernatant turbidity, dewatered cake solids content and ZP.

(d) Interaction between conditioning polymers and sludge flocs

In order to examine the interaction between chitosan polymers and the sludge flocs, the Fourier Transform Infrared (FTIR) spectra of the synthetic sludge system before and after conditioning were analysed and presented in Figure 5.9. It is evident that there are some similarities in these spectra, especially the two major infrared absorption bands at 3270–3340 cm^{-1} and 1630–1640 cm^{-1} observed for both unconditioned and conditioned sludge as shown in Figures 5.9(a)–(d). As discussed in Section 4.3, the former band corresponds to the O–H stretching vibration of alcohols and carboxylic acids while the latter is assigned to the C=O stretching band. With increasing dosage of chitosan till 20 g/kg, a relatively sharper band is found near 2910 cm^{-1} (see Figure 5.9(d)), which is close to the reference band 2900 cm^{-1} often used in the literature to analyse chitin and chitosan (Brugnerotto et al. 2001). This band however overlaps with the CH_2 stretching band from cellulose and yeast (see Figure 4.7 in Chapter 4), which must be examined with care when making any interpretation of interaction between the adsorbing polymers and the sludge flocs.

A more obvious difference can be seen for the fingerprint set of distinct bands between 1030 and 1430 cm^{-1} at the dosage of 20 g/kg. The increased intensities for these bands in Figure 5.9(d) can be attributed to a number of characteristic interactions of the adsorbing polymers with the C–O stretching of the alcohols, esters, ethers and carboxylic acids of the conditioned sludge system, in addition to the C–N stretching of amines in chitosan polymers and yeast. The magnitudes of the characteristic bands increased with increasing conditioner dosage indicating a stronger interaction between chitosan polymers and the sludge system. This may be related to the adsorption of the cationic polymers onto the anionic surfaces of sludge which results in the change of molecular stretching and bending within the sludge structure.

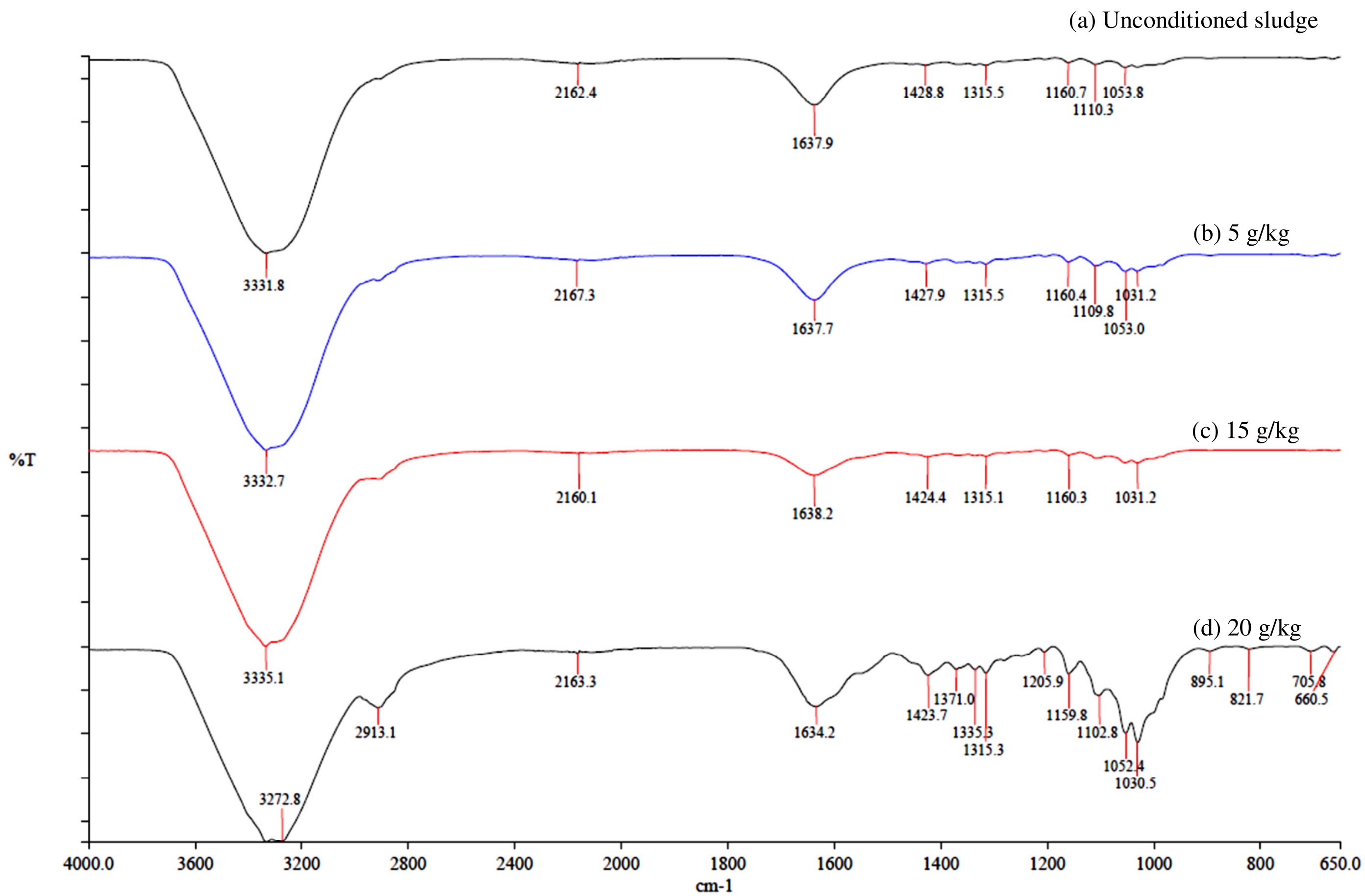


Figure 5.9 FTIR spectra of unconditioned and conditioned sludge at different chitosan dosages

5.3.2 Effect of organic and inorganic compounds as conditioning aids

A comparison of CST results was made between the AD sludge and synthetic sludge systems when both were conditioned with different organic polyelectrolytes and inorganic metal salts or cations. As presented in Figure 5.10, although both sludge systems showed comparable trends of dewaterability with different types of conditioner to some extent, the degree of dewaterability varied notably for the trivalent metal cations and cationic polyelectrolytes. Compared with the control measurement (without conditioning aids), addition of sodium chloride and magnesium chloride reduced the CST marginally for both sludge systems. Meanwhile, synthetic sludge conditioned with aluminium chloride, ferric chloride and few cationic polyelectrolytes (i.e., the polyacrylamide copolymer PAC, medium MW and low MW chitosans) demonstrated superior dewaterability where the CST values reduced by 91–95%. When conditioned in AD sludge, the CST values reduced by 41–62% for aluminium chloride, ferric chloride, EMA 8845 and PAC. The lack of proteins and lipids which are the two important gelling agents responsible for bad sludge dewaterability in synthetic sludge preparation, as suggested by Baudez et al. (2007), could be the reason of discrepancy. However, chitosan conditioning significantly reduced the CST of the AD sludge by 83% and 74% for the medium MW and low MW chitosans, respectively.

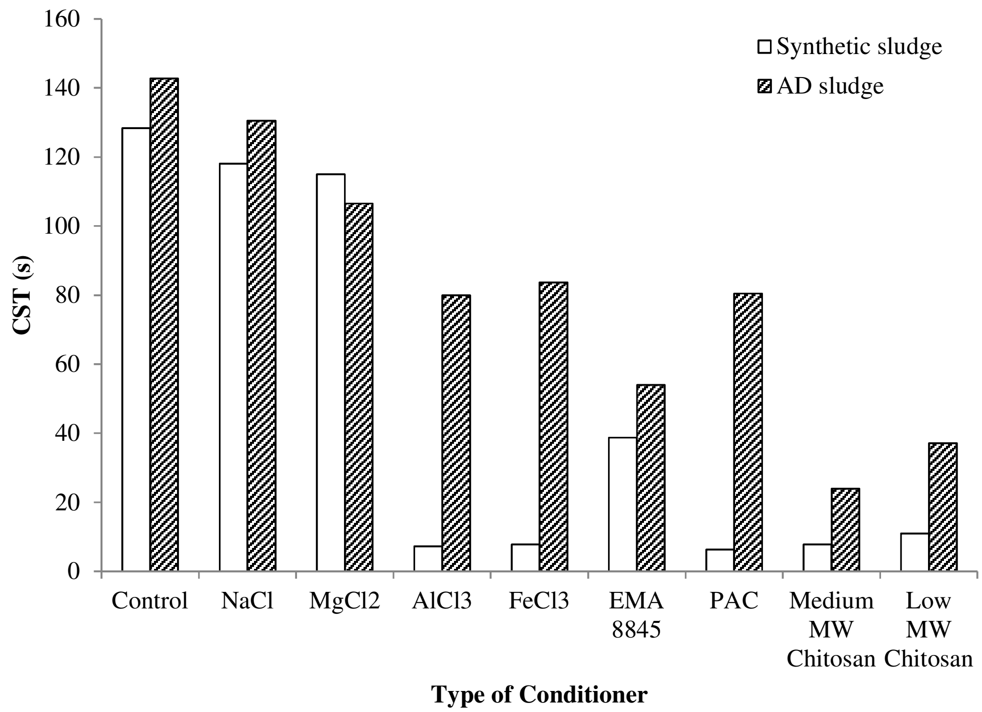


Figure 5.10 Comparison of sludge dewaterability measured by CST between synthetic sludge[1] and AD sludge[2] with different types of conditioner

As found in this work, the trivalent metal cations (Al^{3+} and Fe^{3+}) and cationic polyelectrolytes generally improved the sludge dewaterability in both the AD sludge and synthetic sludge systems. According to the classical Double Layer or Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the addition of cations is believed to improve sludge dewaterability by increasing the solution ionic strength and compressing the double layer, thereby improving the dewatering properties (Sobeck and Higgins 2002, Lau et al. 2014). Little improvement however was observed for the sludge conditioned with the monovalent sodium ion, Na^+ as it lacked binding role within the sludge floc. Sludge conditioning with the divalent magnesium ion, Mg^{2+} showed slightly better dewaterability due to the possible bridging of divalent charges creating a stronger floc matrix as proposed by the Divalent Cation Bridging (DCB) theory (Sobeck and Higgins 2002). For Al^{3+}, Fe^{3+} and the cationic polyelectrolytes, extensive network bridging may occur due to the presence of more cationic charges from the trivalent cations and more cationic sites on the polyelectrolytes. The

[1] Conditioned at 15 g/kg for all conditioners
[2] Conditioned at interpolated dosage of 15 g/kg for cationic polyelectrolytes and 20 g/kg for cations

chloride ions, Cl^{-} from the metal salts may always be regarded the spectator ions in the charge neutralisation reaction. Aluminium and ferric salts are widely used as coagulants in wastewater treatment. In theory, they form cationic hydrolysis products that are strongly adsorbed on negatively charged particles and can give effective destabilisation (Renault et al. 2009).

The FTIR spectra in Figure 5.11 reveal that the fingerprint region for the set of bands between 1030 and 1430 cm^{-1} showed increased intensities when synthetic sludge was conditioned with different types of conditioner at a fixed dosage of 15 g/kg. Compared to the spectrum of unconditioned sludge in Figure 5.11(a), it was found that the interactions at the fingerprint region were not specific to sludge–chitosan alone, but applied to the other effective cationic polyelectrolytes and trivalent cations (see Figures 5.11(b)–(e)). The most significant increases of band intensity were attained for the sludge conditioned with aluminium chloride and ferric chloride as shown in Figures 5.11(d) and (e). The enhanced C–O and C–N stretching at this region pointed to the significance of electrostatic adsorption as a result of charge neutralisation between the cationic conditioning aids and the anionic sludge surfaces.

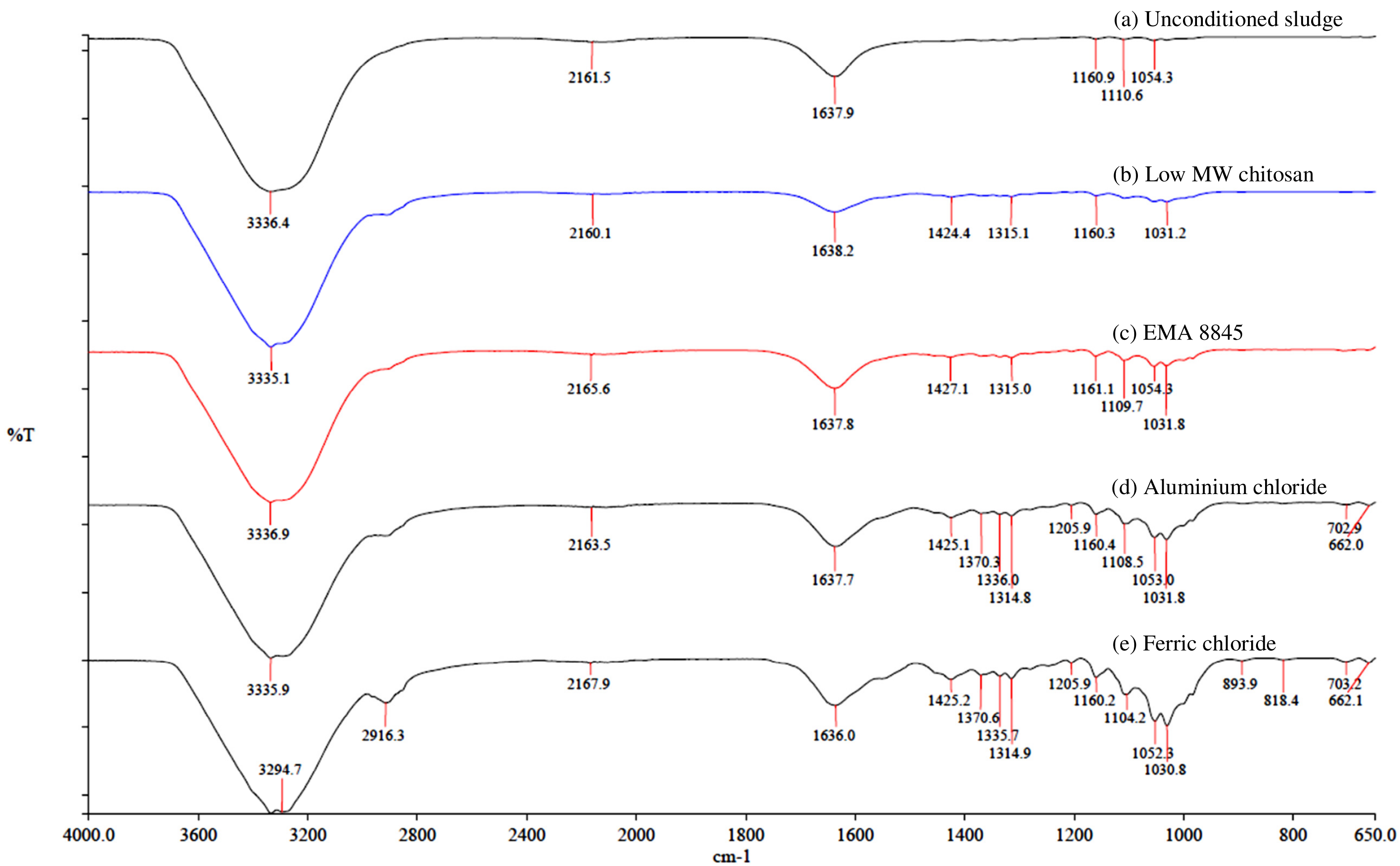


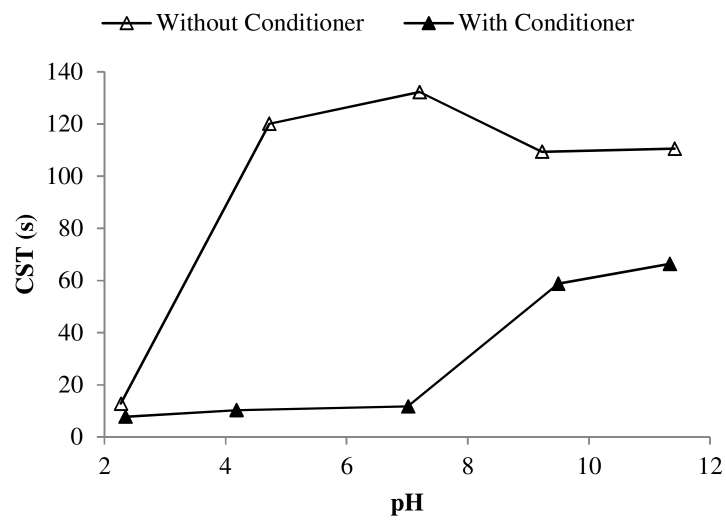
Figure 5.11 FTIR spectra of sludge conditioned with different types of conditioner

5.3.3 Effect of conditioning pH

By changing the pH of the synthetic sludge system with either hydrochloric acid (HCl) or sodium hydroxide (NaOH) during conditioning experiments, Figure 5.12 gives a remarkable account of change in dewaterability as measured by CST, supernatant turbidity and cake solids content with the variation of ±0.3 in pH values from duplicate measurements. Without addition of chitosan conditioner, sludge treated with hydrochloric acid alone showed enhanced dewaterability significantly by reducing the CST to 12.8 s at pH 2.3, as shown in Figure 5.12(a). Figure 5.12(c) indicates high solids content of 25.4% found at this favourable pH after filtration dewatering. Treating sludge with acid (lowering pH) has been reported effective in improving dewatering because it can remove EPS from sludge surfaces (Chen et al. 2001), cause cell disruption (Erdincler and Vesilind 2000), and minimise the ionisation of functional groups (hence the negative charges) on sludge surfaces (Liao et al. 2002). The turbidity of the supernatant, however, was not significantly improved at pH 2.3 in this study, recording 1238.1 NTU from Figure 5.12(b), probably due to the release of intracellular material as a result of cell disruption. Lack of flocculation within the synthetic sludge system (without chitosan conditioning) may also cause more tiny particles to remain suspended in the supernatant after 30 minutes settling, resulting in high turbidity.

A separate study on sludge conditioning with acetic acid alone found no improvement in sludge dewaterability. The lowest pH was attained at 4.0 with CST value of 116.7 s. This is understandable since acetic acid is a weak acid with very low dissociation constant (K_a = 1.8 × 10^{-5}) compared to strong hydrochloric acid. Therefore it can only partially ionise in aqueous solution, making it ineffective for dewatering. As the pH was raised to 4.0 and above in the absence of conditioner, the CST values remained relatively high between 120 and 130 s but alkaline treatment at pH 9.0 and above showed about 16–17% reduction in CST compared to the one at pH 7.2. However, changes in supernatant turbidity and cake solids content were not significant for the sludge system at pHs other than 2.3.

(a)



(b)

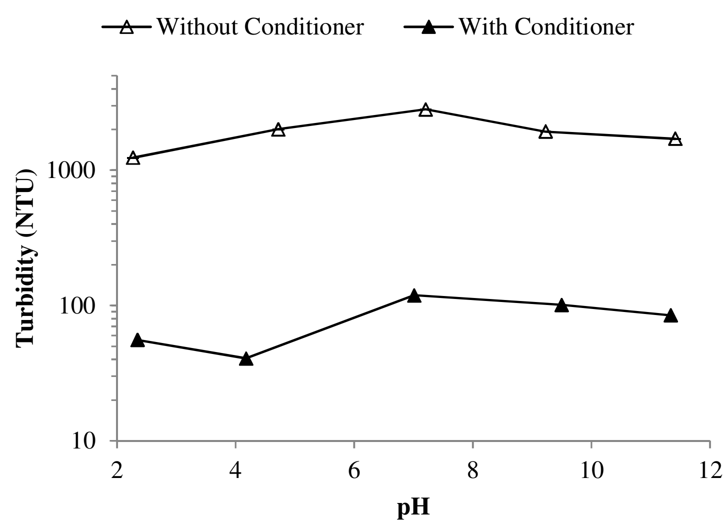


Figure 5.12 Effect of pH on sludge dewaterability with conditioner and without conditioner as measured by (a) CST, (b) turbidity, and (c) cake solids content

(c)

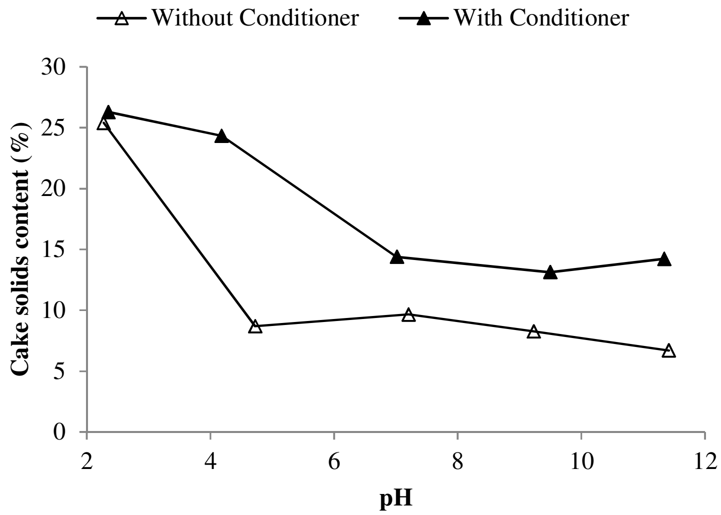


Figure 5.12 Effect of pH on sludge dewaterability with conditioner and without conditioner as measured by (a) CST, (b) turbidity, and (c) cake solids content (continued)

With addition of a fixed dosage of 15 g/kg chitosan conditioner, it can be observed from Figure 5.12 that the lower the pH value was, the better the dewaterability results were recorded. The optimum dewaterability was attained at pH 2.3 with CST 7.8 s, turbidity 55.6 NTU and filtered cake solids content 26.3%. The CST values between pH 2.3 and 7.0 varied slightly between 7.8 and 11.8 s which indicated generally good dewaterability at this range of pH for chitosan conditioning. Under alkaline condition, however, the CST values increased but they were still about 40–46% lower than the ones of unconditioned sludge at respective pHs as illustrated in Figure 5.12(a). The changes in supernatant turbidity and cake solids content were less significant when the sludge was conditioned with chitosan at pH 7.0 and above (see Figures 5.12(b) and (c)). Compared with unconditioned sludge, chitosan conditioning reduced the turbidity by approximately two orders for the range of pH studied.

pH is known to affect the ionisation of the functional groups of organic polymers and to determine the surface charges carried by the sludge particles (Christensen et al. 2015). Chitosan conditioner applied in this study is a pseudo-natural cationic polymer which consists of repeated $–NH_2$ amine groups along its polymeric structure, with the acid ionisation constant (pK_a) of approximately 6.5 (Kaseamchochoung et al. 2006). According to Sanin et al. (2011), at pH values lower than the pK_a value, the cationic polymer offers a cationic nature and stretched structure; while above this pH, it presents a neutral nature and coiled structure with less accessibility for effective adsorption. The state of being stretched is important for polymers to be able to effectively bridge the gap between sludge particles. Therefore under the acidic condition applied in the present study, chitosan may dissociate to form positively charged $–NH_3^+$ sites along its stretched structure, leading to enhanced sludge flocculation and dewatering as observed in Figure 5.12.

The interactions between chitosan and the sludge flocs under the acidic, near pK_a and basic conditions were further examined from the FTIR spectra in Figure 5.13. As identified earlier, the fingerprint region for the set of bands between 1030 and 1430 cm^{-1} showed increased intensities at pH 2.5 (see Figure 5.13(a)) compared to those at pHs 6.5 and 10.4 (see Figures 5.13(b) and (c)). There was also a noticeable shift of the wavelength peak from about 2903 to 2924 cm^{-1} when the pH was reduced from 6.5 to 2.5. Shifts of this magnitude in infrared spectra are considered significant according to Rubinson and Rubinson (2000). The interactions between the protonated chitosan at pH 2.5 and the functional groups of sludge may lead to the above transformation of CH_2 stretching band in the range of 2850–3000 cm^{-1} (Rubinson and Rubinson 2000). In addition, a new band appeared near 1550 cm^{-1} in Figure 5.13(a) which may possibly be attributed to the extra N–H bending of the amine groups due to the enhanced stretching of chitosan at low pH. As discussed earlier in this section, the amine groups on chitosan can be protonated at pH lower than the pK_a value of 6.5. The more acidic the pH is, the more the protonated $–NH_3^+$ sites may appear which result in higher degree of stretching or extension of the chitosan polymeric structure for the bridging of sludge particles. The appearance of the N–H bending band near 1550 cm^{-1} may thus be expected as more $–NH_3^+$ sites in the chitosan chain interact electrostatically with the negatively charged sites of the sludge.

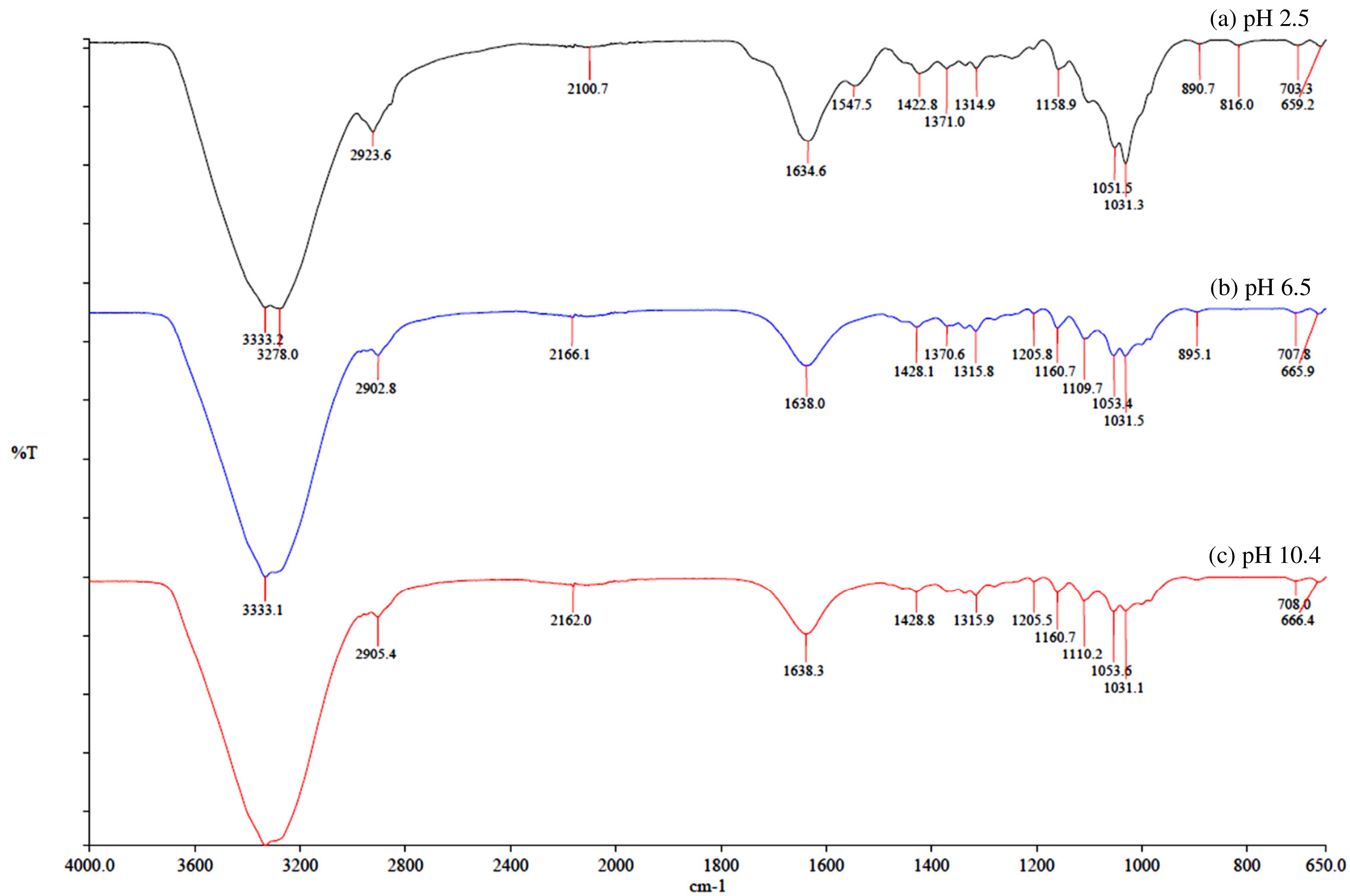


Figure 5.13 FTIR spectra of conditioned sludge at different pHs

The comparative study of pH effect without and with conditioner clearly suggested that different mechanisms may govern the sludge coagulation and flocculation under the effect of pH. At very acidic (pH 2.3) and very basic (pH 11.4) experimental conditions in the absence of conditioner, both acid and alkaline treatments may cause desorption of EPS and disruption of cells which enhanced the dewaterability to some extent, without significant improvement in reducing turbidity. In addition, pH affects the charges of the functional groups on the sludge causing neutralisation which facilitates coagulation and release of water at low pH, as indicated by the low CST and high cake solids content at pH 2.3 in this study. With addition of chitosan, the findings suggest that both charge neutralisation and polymer bridging mechanisms are important to enhance sludge flocculation and dewatering at low pH while the deficiency of ionised amine groups at pH 7.0 may reduce the capture of fine particles as indicated by the increase in turbidity and decrease in cake solids content at pH 7.0. Above pH 7.0, presumably only non-electrostatic interactions in adsorption and polymer bridging are dominating where the sludge dewaterability is moderately improved.

5.3.4 Effect of conditioning temperature

Conditioning temperature has a minor effect on sludge dewatering for the range applied in the present study at a fixed dosage of 20 g/kg chitosan. Figure 5.14 shows that the CST value decreased to a minimum of 4.7 s at 35°C and increased slightly to 6.3 s at 55°C. Increase of temperature from 25°C to 35°C marginally reduced the CST value probably due to the thermally induced molecular diffusion which enhanced the interactions between the sludge and the conditioner. Another possible explanation could be that the thermal treatment causes the solubilisation of EPS and disruption of cells, providing more negatively charged binding sites for the polymer to establish stronger bridging among the sludge flocs (Guan et al. 2012). Further increase of temperature increased the CST but the overall impact of temperature on the CST result was less profound in the temperature range investigated in this study (25–55°C). FTIR spectra also revealed no change in band shift or intensity for sludge conditioned at different temperatures as shown in Figures 5.15(a)–(d). It is possible that the presence of eddy diffusion and nonuniform flow (orthokinetic motion) as a result of mixing during polymer conditioning overwhelms molecular diffusion (perikinetic motion) where the latter is more affected by temperature (Droste 1997).

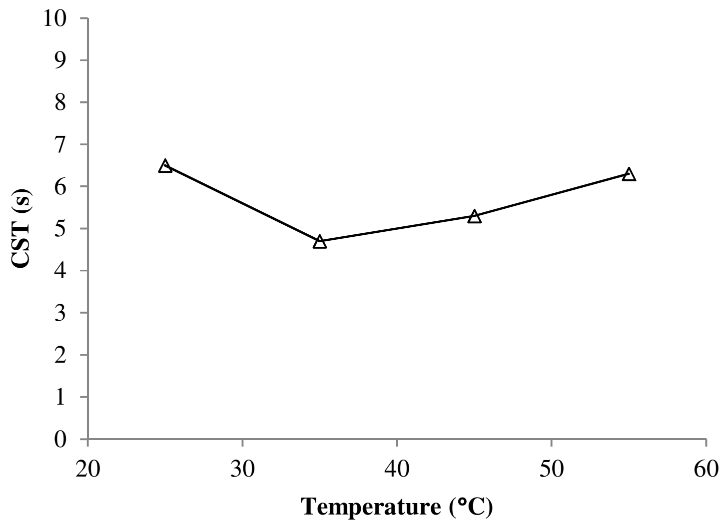


Figure 5.14 Change in CST with temperature for synthetic sludge conditioned with 20 g/kg chitosan

5.3.5 Effects of mixing speed and mixing time during flocculation

Sludge conditioning process involves two mixing steps. The first step is often called coagulation which requires short detention time and rapid mixing. Transport interactions between sludge particles and conditioning chemicals during initial dosing and rapid mixing are hence less important than the subsequent flocculation step (Droste 1997). However high-shear condition should be avoided as it can destroy the structure of the sludge. In this study, the coagulation reaction was fixed at 300 rpm mixing in one minute where all sludge particles were suspended uniformly throughout the bulk solution.

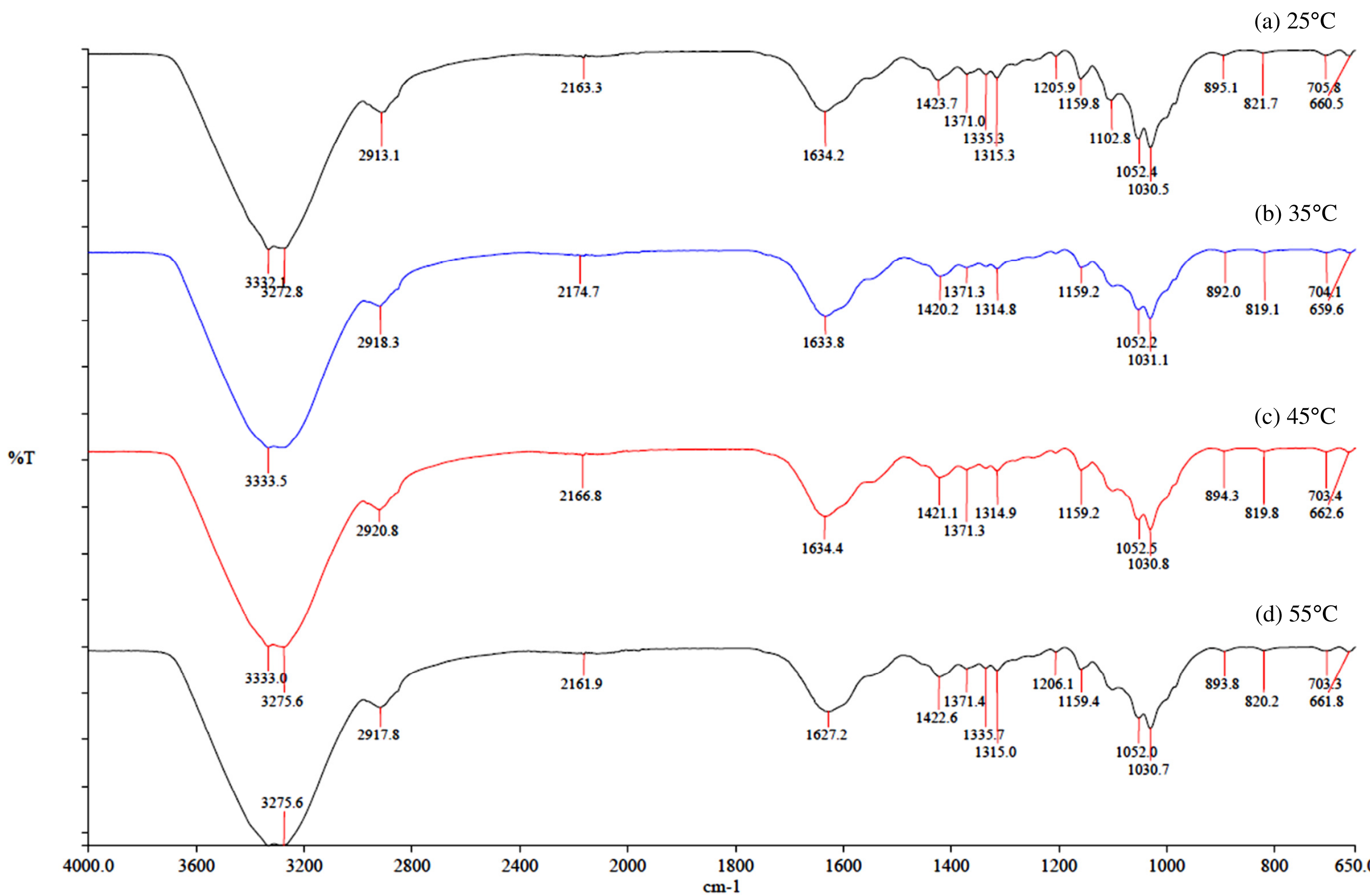


Figure 5.15 FTIR spectra of conditioned sludge at different temperatures

For the second step–flocculation to occur effectively, the effects of mixing speed and mixing time were studied. A lower degree of mixing is required in the flocculation step to promote particle contact yet prevent breakage of the large flocs formed from the coagulation step. Figure 5.16 shows that at a fixed mixing time of 300 s, as the mixing speed increased from 0 rpm to 300 rpm, the CST reduced to a minimum of 19.2 s at 50 rpm then it increased again with increasing speed for sludge conditioned at 10 g/kg chitosan. It is likely that the sludge flocs formed at 10 g/kg were not resilient enough to withstand the excessive shearing causing floc disintegration. In Figure 5.17, the change of ZP from –14 mV at 0 rpm to –18 mV at 300 rpm further suggests that the intense mixing may have destroyed the sludge structure causing deterioration in sludge dewaterability with increased surface charge repulsion. Fluctuations in supernatant turbidity and cake solids content as a function of mixing speed did not draw any meaningful discussion.

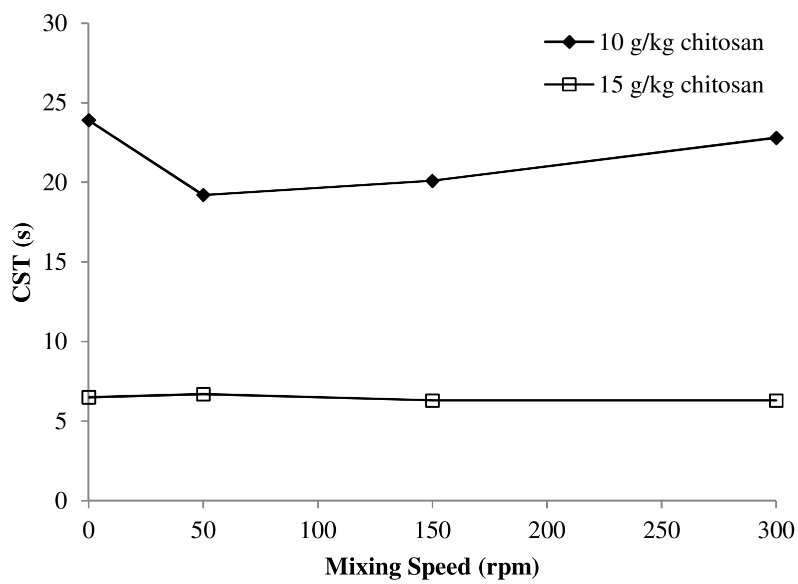


Figure 5.16 Change in CST at different mixing speeds at the flocculation step

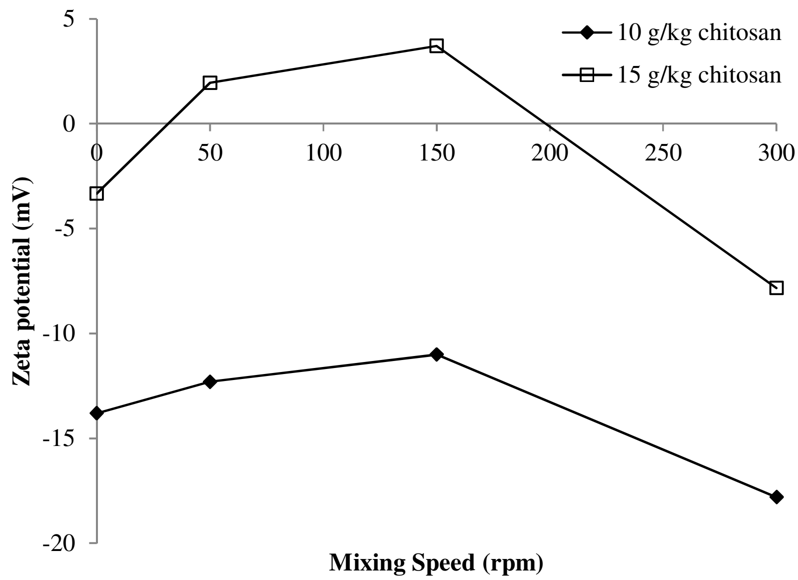


Figure 5.17 Change in zeta potential at different mixing speeds at the flocculation step

On the other hand, no significant change in CST was observed for sludge conditioned at 15 g/kg chitosan as shown in Figure 5.16. But similar trend of change in ZP with increasing mixing speed is observed in Figure 5.17 for both dosages. Restabilisation occurred where ZP became more negative at 300 rpm indicating increased surface charge repulsion upon excessive mixing. This degree of change did not affect much on the CST values as the polymer bridging mechanism may still be dominating. When measured by supernatant turbidity and cake solids content, higher mixing speed dampened the dewatering performance with increased turbidity and reduced cake solids content at 300 rpm. From physical observation, the supernatant became more turbid and smaller sludge flocs were formed at higher level of mixing. Too much shearing prevents effective polymer bridging between the sludge and the conditioner, resulting in formation of smaller flocs or floc disintegration. This, in turn, increases turbidity in supernatant as well as sludge surface-to-volume ratio which subsequently reduces the cake solids content with more bound water attached to the sludge surface.

Meanwhile, it can be seen from Figure 5.18 that increase of mixing time did not significantly affect the CST values especially at the dosage of 15 g/kg chitosan when the conditioning experiments were conducted at a slow mixing speed of 50 rpm. This may imply that the coagulation step effectively agglomerates the sludge particles at that dosage and thus additional detention time in flocculation gives less impact to the sludge dewaterability. However at the dosage of 10 g/kg chitosan, slow mixing for 60 s reduced the CST from 25.0 s to 19.4 s and additional mixing time was less important to enhance dewatering. Furthermore, the turbidity was not significantly reduced and the cake solids content decreased as the mixing time increased (see Figures 5.19(a) and (b)). The turbidity was generally high at this dosage because the resulting charge neutralisation was incomplete as seen from the ZP values in Figure 5.19(c). Increase of ZP from –22 mV to –11 mV was observed during the first 60 s slow mixing and the values remained almost constant (without reaching a zero ZP value) with extended mixing. In addition, the extended shearing may cause the sludge flocs to break up and release fine particles back to the bulk solution, presumably less resilient flocs were formed at this dosage. The breakage of flocs causes turbidity and reduces the cake solids content due to the increased surface-to-volume ratio.

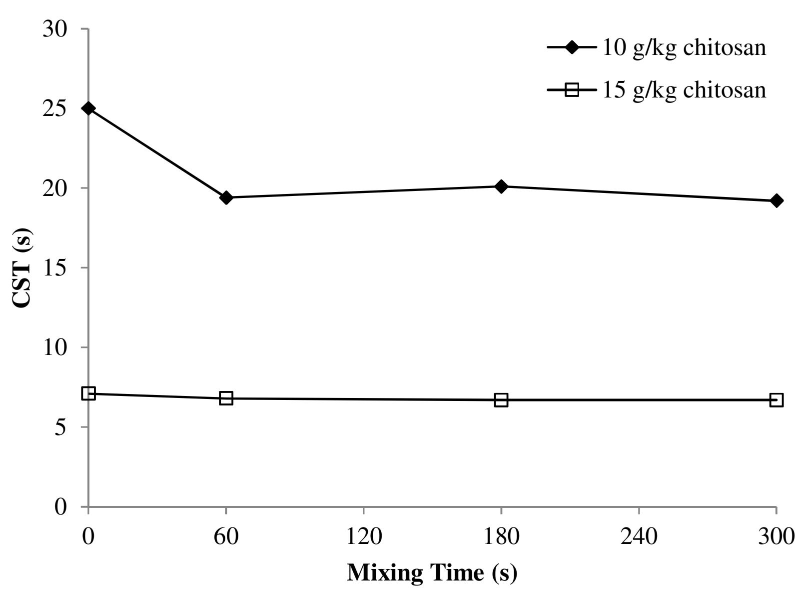


Figure 5.18 Change in CST at different mixing times at the flocculation step

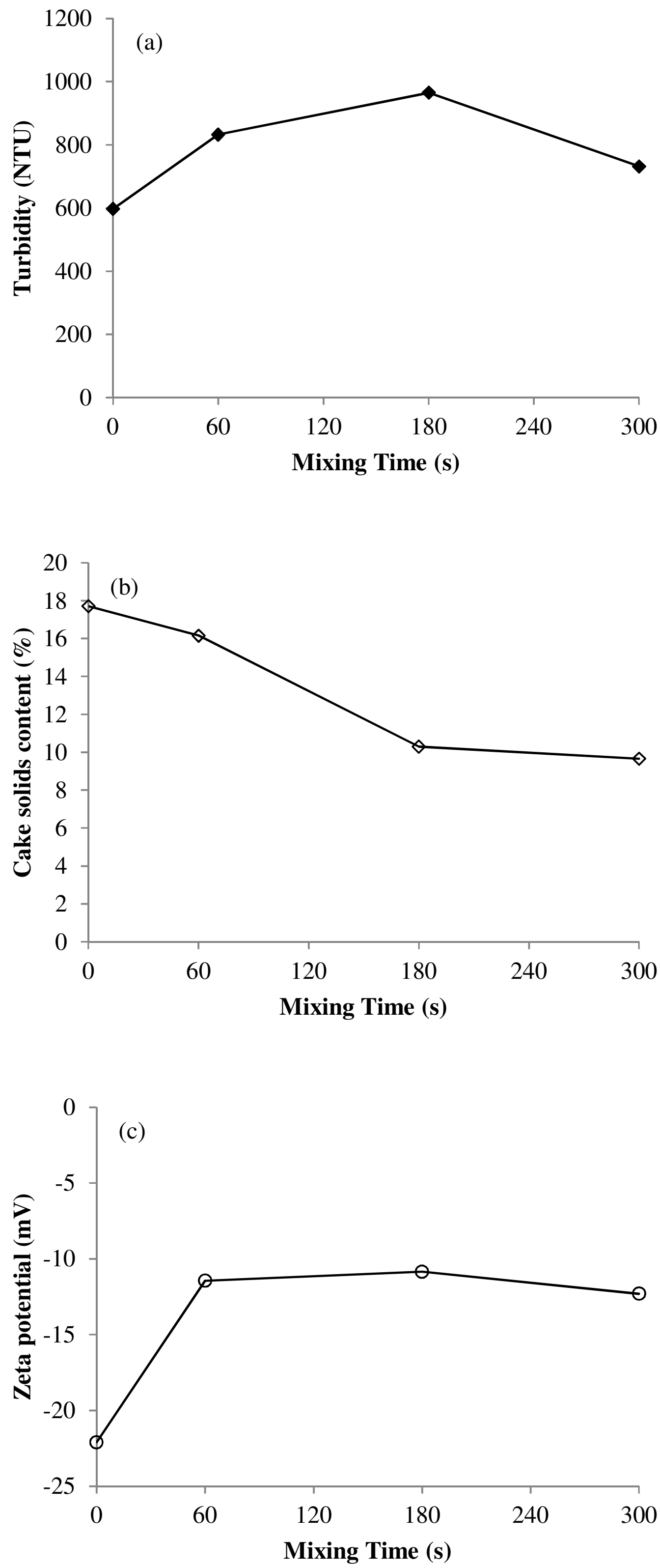


Figure 5.19 Effect of mixing time on (a) turbidity, (b) cake solids content, and (c) zeta potential at 10 g/kg chitosan

5.4 Conclusion

In the present study, adsorption and charge neutralisation are the leading mechanisms in sludge conditioning where the cationic organic or inorganic molecules adsorb onto the sludge surface and neutralise the charges causing effective destabilisation of the sludge system. Charge neutralisation is evident from the change of ZP values from negative to near zero at increasing polymer dosage, accompanied with enhanced sludge dewaterability. In addition, extensive network bridging by the trivalent cations and polymer bridging by the organic polyelectrolytes further destabilise the sludge system and flocculate the sludge particles. More bound waters are released (indicated by increased cake solids content) causing enhanced sludge dewatering. Findings from this chapter may be summarised as follows:

- Lower MW chitosan is effective at even very low dosage but higher dosage causes bulky sludge flocs with more trapped water.
- The effectiveness of chemical conditioning can be assessed using CST, supernatant turbidity, dewatered cake solids content and ZP. In this study, the optimal dosage was found at the range of 15–20 g/kg chitosan where the values of CST, turbidity and cake solids content were attained between 6.6–11.0 s, 35.4–40.6 NTU and 24.3–25.3% respectively. ZP measurement provides important information about the conditioning mechanism where charge neutralisation takes place near the optimum dosage with enhanced dewaterability.
- The trivalent metal cations and cationic polyelectrolytes may act as effective coagulants (via charge neutralisation) and flocculants (either polymer or ion bridging) in sludge conditioning and dewatering for both the AD sludge and synthetic sludge systems.
- Low pH is favourable for sludge conditioning as it enhances the ionisation of the amine groups of chitosan and suppresses the negative surface charges carried by the sludge particles.
- Temperature has a minor effect on sludge conditioning process.
- Restabilisation occurs where mixing speed and mixing time increase in the flocculation phase. This is especially true when applied to sludge conditioned

at dosage lower than the optimum where the flocs formed may be less resistant to excessive shearing.

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CHAPTER 6

STUDIES OF RHEOLOGICAL PROPERTIES OF CONDITIONING SYNTHETIC SLUDGE*

6.1 Introduction

It is well known that wastewater and sewage sludge suspensions are invariably non-Newtonian fluids, the shear rate (or strain rate) $\dot{\gamma}$ being non-linearly related to the shear stress τ (Seyssiecq et al. 2003). In the case of dewatering operation, the application of conditioning aids and the resulting biomass of flocs during sludge conditioning process significantly influence the rheology of suspension. The study of sludge rheology provides fundamental information on the characteristics of sludge for optimal conditioning, especially in chemical dosage. However the nonequilibrium nature of the flocculated and coagulated suspensions poses difficulties both from the experimental and theoretical aspects in the studies of sludge rheology, and hence advances in the rheology of suspension have been slow (Tadros 2010). This chapter presents the development of sludge rheological model in synthetic sludge conditioning under different physicochemical and operating conditions which have large implications in wastewater treatment plant. This chapter also attempts to answer how sludge dewaterability and rheology respond relatively to different physicochemical process parameters as compared to those of a typical anaerobic digested (AD) sludge in literature. Correlations linking the rheological properties to the sludge dewaterability parameter under the different physicochemical process parameters in sludge conditioning were examined in order to optimise the chemical dosage.

* A manuscript from this chapter is under preparation for submission to journal.

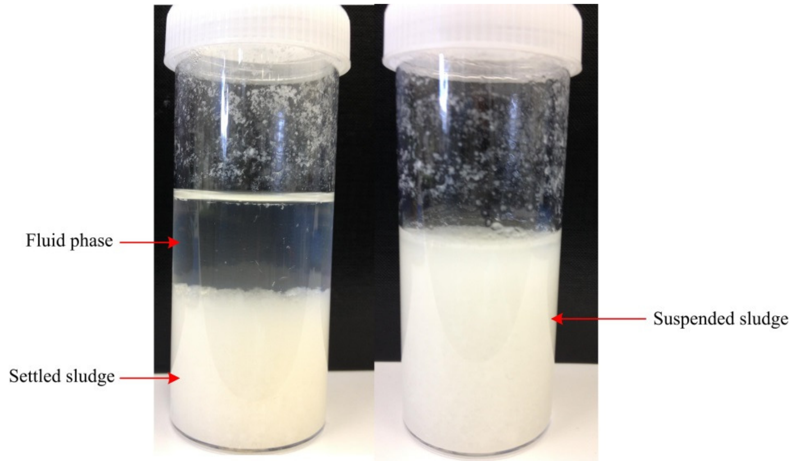
6.2 Materials and Methods

The rheological rotational tests were carried out in controlled shear rate mode, from 0.0001 to 100 s^{-1} in 300 s, using concentric cylinder measuring system which was fitted to the rheometer. The conditioned sludge sample was pipetted into the measuring cell and the measurement was performed using the connecting software commands. During the measurement, the sample was sheared in the gap between two concentric cylinders where the inner cylinder was rotated at a controlled rotation rate. The resistant torque on the cylinder was measured and related to shear stress by the device software in obtaining the rheogram data. Rheograms (also known as flow curves) are plots of shear stress against shear rate. The sludge rheological behaviours were studied under different sludge sampling locations, conditioner dosages, conditioner types, pH, and temperatures, as well as mixing speeds and mixing times. The temperature of the sample in the rheometer was maintained at 25°C in all measurements except for the study of temperature effect.

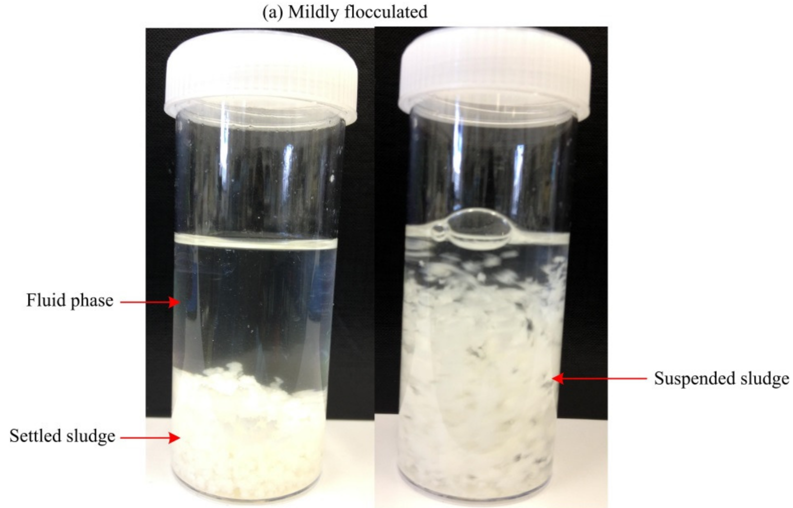
6.3 Results and Discussion

6.3.1 Effect of sludge sampling location on rheology

The rotational tests were first carried out to decide a proper sampling location from the flocculated synthetic sludge system. Specimens were sampled from three locations, namely the fluid phase (the watery supernatant layer), the suspended sludge (the uniformly dispersed sludge suspension) and the settled sludge (see Figure 6.1). The three sampling locations may represent the sludge flow behaviour at different stages during dewatering operation. The study of fluid phase rheology may be related to the pumping of effluent or supernatant back to the primary treatment after dewatering. The study on suspended sludge may inform the sludge flow behaviour during dewatering operation in separation of water (fluid) and sludge flocs. The settled sludge will likely represent the concentrated slurry after flocculation with higher resistance to flow.



(a) Mildly flocculated



(b) Highly flocculated

Figure 6.1 Sampling locations for rheological tests

From Figure 6.2, it was found that the shear stress τ increased non-linearly with shear rate $\dot{\gamma}$ indicating non-Newtonian pseudoplastic flow behaviour for the raw or unconditioned synthetic sludge. The shear thinning behaviour followed the power-law model, $\tau = K\dot{\gamma}^m$ regardless of the sampling location, where K is the consistency index and m is the flow behaviour index. Despite a few outliers found in the rheograms, the data fitted the model reasonably well as indicated by the high correlation coefficients of R^2 given in Table 6.1. The obtained rheological parameters from the fitted model are also presented in Table 6.1. It was found that the flow behaviour index m confirms the non-Newtonian behaviour of sludge sample and it is virtually independent of sampling location.

The findings were consistent with the work of Ayol et al. (2006) as well as Wang and Dentel (2011) where they reported that the various digested sludge samples were satisfactorily modelled by the power-law model with high confidence. For such pseudoplastic fluids, it is difficult to define a single viscosity value as the viscosities are shear-rate dependent as shown in Figure 6.3. For this study, the apparent viscosity decreased to a constant average of 4.2 mPa.s as the shear rate increased to 100 s^{-1} at 25°C. Sanin and Vesilind (1999) modelled a similar pseudoplastic synthetic sludge behaviour and they reasoned that the sludge flocs were broken down into smaller flocs with the increased shear, releasing part of the bound water and reducing viscosity.

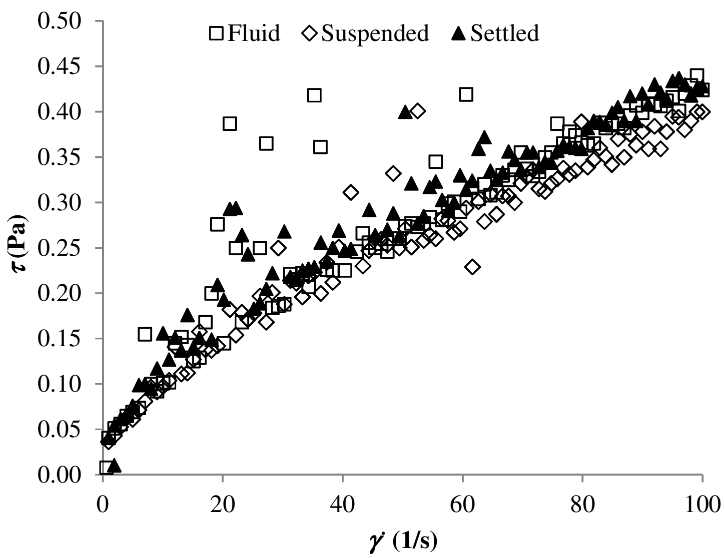


Figure 6.2 Rheograms of raw synthetic sludge sampled at different locations

Table 6.1 Best fit results of the power-law model for raw synthetic sludge at different sampling locations

Sampling location	Consistency index, K (Pa.s^m)	Flow behaviour index, m	R^2
Fluid phase	0.0289	0.5889	0.8959
Suspended sludge	0.0288	0.5661	0.9710
Settled sludge	0.0308	0.5780	0.9020

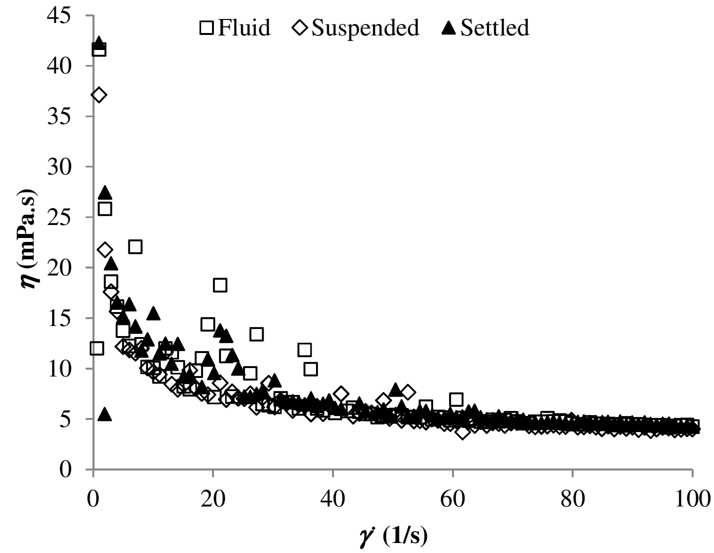
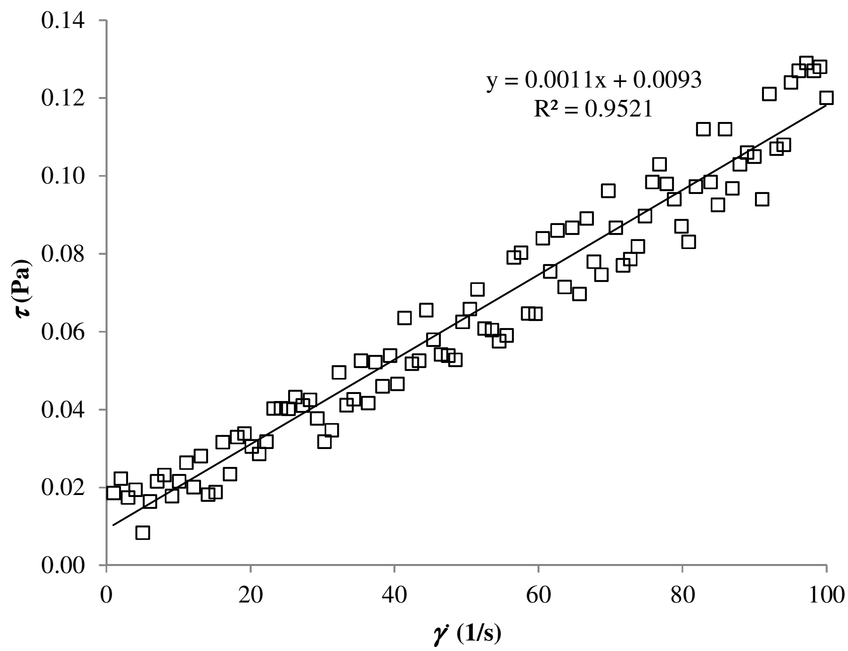
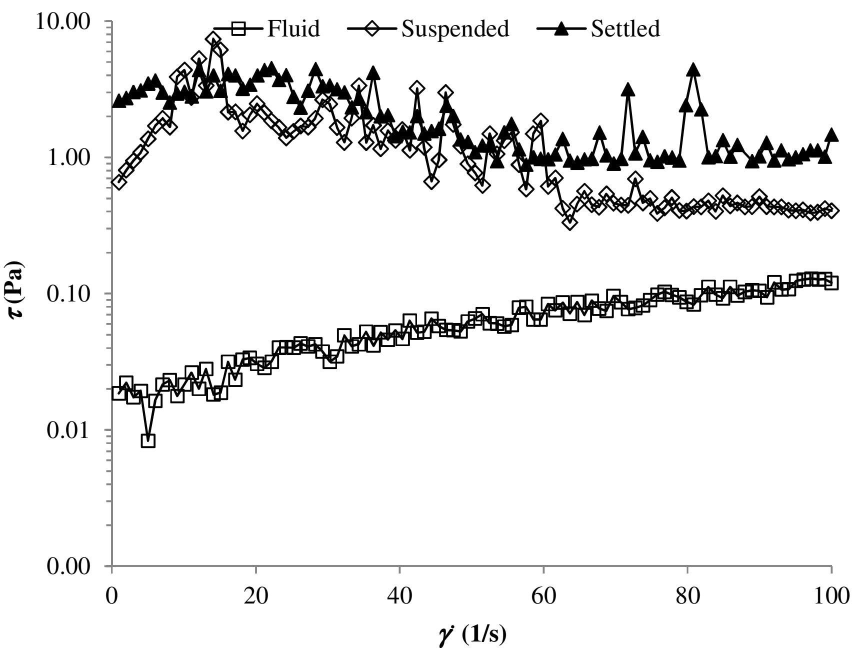


Figure 6.3 Viscosity-shear rate curves of raw synthetic sludge sampled at different locations

Apart from raw sludge, the effect of sampling location on sludge rheology was also studied for conditioned sludge at the dosage of 15 g/kg chitosan. The rheograms were illustrated separately in Figure 6.4 in order to keep the plots readable at different orders of shear stress. As presented in Figure 6.4(a), the sludge sampled from the fluid phase exhibited an excellent fit of the Bingham model, $\tau = \tau_0 + \eta\dot{\gamma}$ over the range of shear rate up to 100 s^{-1} with the R^2 value of 0.9521. The constant plastic viscosity (or Bingham viscosity), η value of 1.1 mPa.s is slightly higher than that of pure water, i.e., 0.89 mPa.s at 25°C, which suggests that there may be little amount of residual matter or polymer which increase the supernatant viscosity at this dosage. The fluid phase viscosity of conditioned sludge (1.1 mPa.s) was lower than the one of raw synthetic sludge (4.2 mPa.s) as the incomplete solid-liquid separation in the raw sludge system caused significant amount of colloidal particles remained suspended in the fluid phase and induced more resistance to flow.



(a) Fitting of fluid phase rheology to the Bingham model



(b) Comparison of rheograms in logarithm scale

Figure 6.4 Rheograms of conditioned synthetic sludge sampled at different locations

Figure 6.4(b) shows that the polymer conditioned sludge samples exhibited non-Newtonian behaviour, with peak values in the rheograms for both the suspended sludge and settled sludge. Under these conditions, the flow was difficult to model with the commonly known sludge models such as the power-law, Bingham, or Herschel and Bulkley models over the range of applied shear rate. This is likely due to the presence of high solid volume fraction in the sludge which deters a characteristic fluid flow. Ayol et al. (2006) attributed this phenomenon as a polymer-sludge network strength that is eventually disrupted under increasing shear. They proposed that when the commonly used models do not account for this behaviour, the rheological data may be evaluated by two alternative means: first, using peak stress values; and second, using the network strength energy.

It is also clear from Figure 6.4(b) that the suspended sludge and settled sludge showed an apparent yield stress value which may be obtained by an extrapolation of the linear portion of the curve to $\dot{\gamma} = 0$ (Tadros 2010). In the present study, the extrapolation was performed at very low shear rates before the first peak value using the Bingham model, as shown in Figure 6.5. The rheological parameters derived from the Bingham model are listed in Table 6.2. Similar practice to extrapolate the linear portion of the rheogram to the ordinate to obtain the assumed true value of the yield stress has been reported by Baudez et al. (2013) in a rheological study with AD sludge. The results of Table 6.2 show that the Bingham viscosities of the suspended sludge and settled sludge were identical, which were two orders higher than the one of the fluid phase. Meanwhile the increase of yield stress from 0.0093 Pa in the fluid phase to 2.3461 Pa for the settled sludge indicates a notable increase in the structure resistance to flow as a result of sludge concentration. This also implies an increase of the sludge’s network strength. The presence of yield stress has an important impact on various sludge treatment operations such as dewatering, storage, transportation, agricultural use, land filling, and incineration (Eshtiaghi et al. 2013).

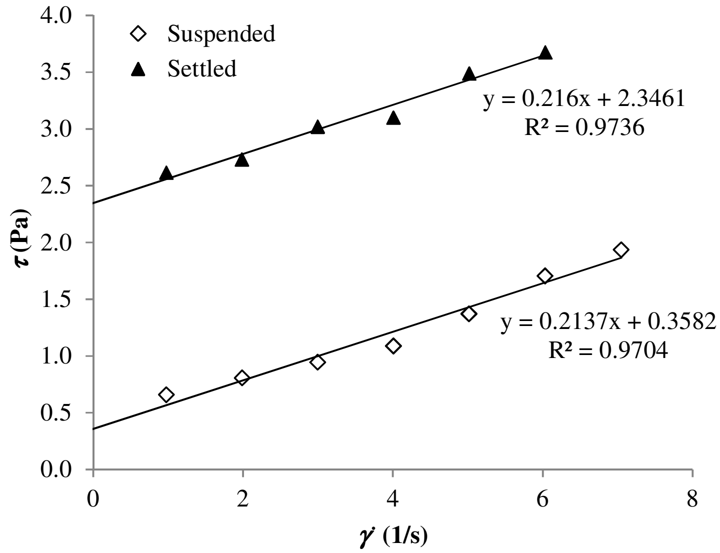


Figure 6.5 Extrapolation to obtain apparent yield stress at low shear rates for suspended sludge and settled sludge

Table 6.2 Rheological parameters for conditioned synthetic sludge at different sampling locations

Sampling location	Bingham viscosity[a] (mPa.s)	High-shear viscosity[b] (mPa.s)	Yield stress (Pa)	R^2
Fluid phase	1.1	1.2	0.0093	0.9521
Suspended sludge	213.7	4.1	0.3582	0.9704
Settled sludge	216.0	14.7	2.3461	0.9736

[a]The Bingham model is fitted at low shear rates for the suspended sludge and settled sludge (see Figure 6.5).

[b]The high-shear viscosity is taken from the apparent viscosity at the shear rate of 100 s^{-1} (see Figure 6.6).

Figure 6.6 shows that the suspended sludge and settled sludge demonstrated pseudoplastic flow behaviour with decreasing viscosity till a near constant viscosity plateau at high shear rates. The high-shear viscosity increased from the fluid phase to the settled sludge as well, as given in Table 6.2. Both viscosity and yield stress values found in this study may be used as a relative indicator for the network strength of the sludge flocs formed from polymer conditioning. Significant fluctuations in apparent viscosity with increasing shear rate were observed for the suspended sludge possibly due to the interaction between the bulk fluid phase and the sludge floc particles in dispersion. Therefore it is decided that the sludge should be sampled from a well-mixed suspension, i.e., the suspended sludge in this study, in order to explore the sludge rheological behaviour in the presence of fluid-floc interaction. This is also in view of the proposition of Seyssiecq et al. (2003) that rheological measurements on suspensions must remain as bulk properties due to the spatial variations in shear rate and shear stress calculated in the gap of measuring geometry. Thus all samples for the following studies were taken from the sludge in suspension after conditioning unless stated elsewhere.

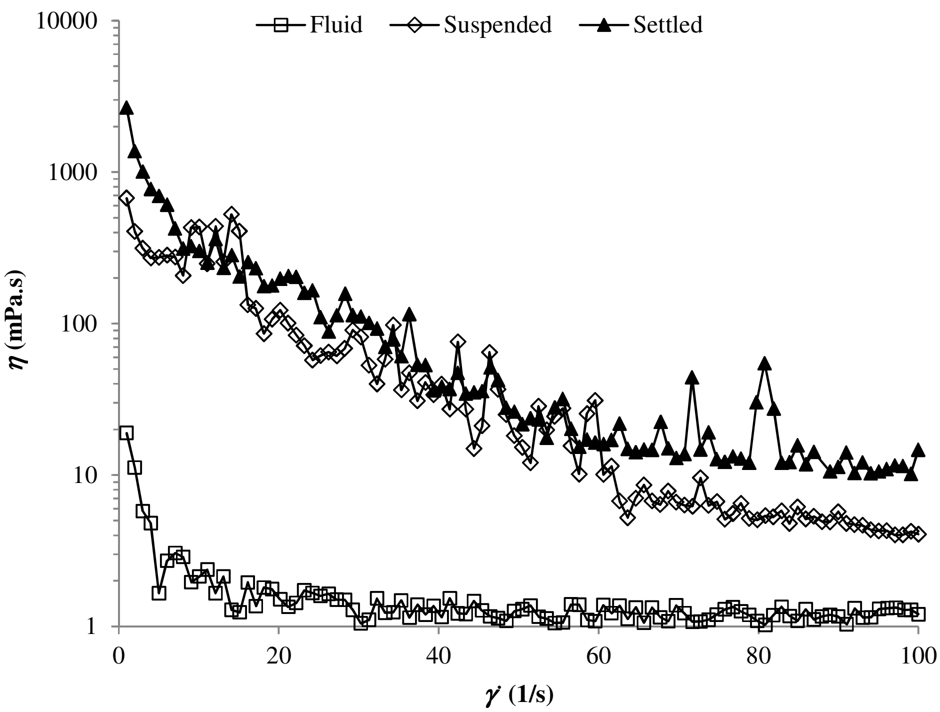


Figure 6.6 Viscosity-shear rate curves of conditioned synthetic sludge sampled at different locations

6.3.2 Effect of chitosan conditioning and its optimum dosage for suspended sludge

As discussed in Section 6.3.1, the raw synthetic sludge has been identified as a shear thinning fluid without any significant yield stress. The addition of conditioner introduced certain amount of yield stress to the suspended sludge. The rheograms of conditioned sludge at different chitosan dosages are presented in Figure 6.7. The range of chitosan dosages was selected as per industrial wastewater sludge treatment practice. Figure 6.7 shows that the conditioned sludge at higher chitosan dosage experienced higher resistance to flow as indicated by the increase in shear stress magnitude. At the dosages of 10–15 g/kg chitosan, it can be observed that the shear stress increased to a peak value then gradually declined to a plateau with increasing shear rate. It is inferred that the sludge flocs experienced breakage and exhibited fluctuations in the flow curves. As for the very high dosages of 20–30 g/kg chitosan, the curves remained almost flat throughout the whole shear rate range applied.

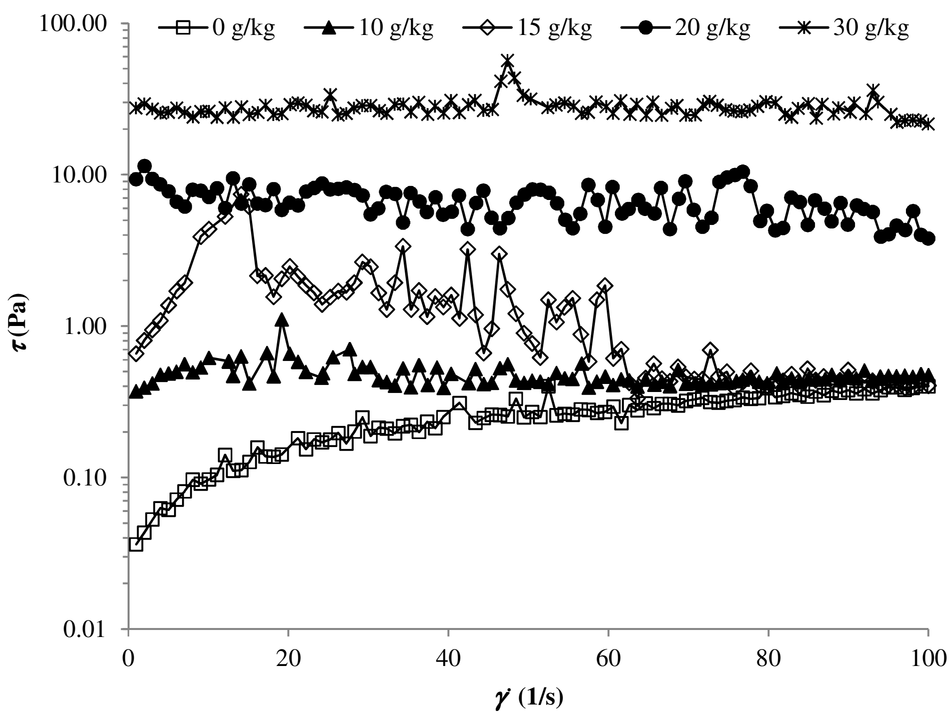


Figure 6.7 Rheograms of conditioned sludge at different chitosan dosages

Tadros (2010) explained that the three dimensional (3-D) network of the particles formed at high volume fraction of the suspension may be broken into smaller units of flocculated spheres (the flocculi) under shear. Accordingly, more than one peak can be observed from the rheogram of flocculated suspensions such as the one observed for the dosages of 10–15 g/kg chitosan in this study. The first peak may indicate the network strength of the bigger flocculated sludge flocs, and the following peak(s) may then indicate the flocculi (due to breakage after initial shear) which can withstand further shear forces. To obtain a reasonable estimate of the apparent yield stress value, the rheograms for conditioned sludge at 10–15 g/kg chitosan from Figure 6.7 were modelled at low shear rates before the first peak with the Bingham model and the best fit results are given in Table 6.3. This model failed to represent the non-Newtonian behaviour of the conditioned sludge at 20–30 g/kg chitosan. The sludge suspension did not exhibit any known behaviour of fluid model at these dosages due to the high solids fraction in the flocculated sludge. The corresponding yield stress values were thus obtained by simple extrapolation at low shear rates.

Table 6.3 Rheological parameters obtained at different chitosan dosages

Dosage (g/kg)	High-shear viscosity (mPa.s)	Yield stress (Pa)	First peak height (Pa)	R^2
0	4.0	–	–	0.9710
10	4.8	0.34	1.11	0.9635
15	4.1	0.36	7.41	0.9704
20	38.0	7.40	11.41	–
30	216.1	25.86	56.66	–

Remark: Unconditioned sludge is a pseudoplastic fluid without significant yield stress; conditioned sludge at 10–15 g/kg was fitted with the Bingham model at low shear rates; conditioned sludge at 20–30 g/kg was difficult to model with any sludge models and yield stress was obtained by simple extrapolation at low shear rates.

The viscosity-shear rate curves shown in Figure 6.8 indicate that the pseudoplastic flow behaviour of sludge was affected by the conditioner dosage. A pseudo-Newtonian region was found at high shear rates, corresponding to the value of high-shear rate viscosity, similar to the ones in Section 6.3.1. According to Seyssiecq et al. (2003) and Eshtiaghi et al. (2013), the rheological property of sludge can be better described by a single parameter of limiting viscosity due to the non-Newtonian behaviour of sludge. The concept of limiting viscosity is similar to the one of high-shear viscosity where the apparent viscosity becomes almost constant at high shear rates as shown in Figure 6.8. This allows proper comparison of viscosity for different pseudoplastic sludge samples. In this study, the viscosity values were obtained at the shear rate of 100 s^{-1} (termed as high-shear viscosity) and given in Table 6.3 together with other rheological parameters for comparison of chemical dosage effect.

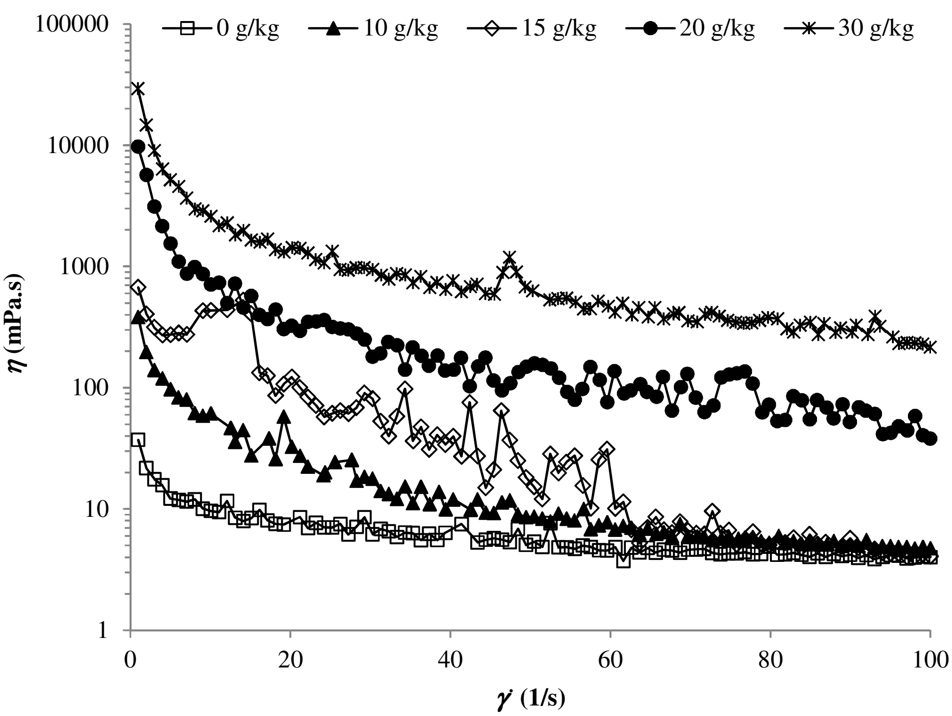


Figure 6.8 Viscosity-shear rate curves of conditioned sludge at different chitosan dosages

Table 6.3 reveals that the high-shear viscosities were almost similar recording 4.0–4.8 mPa.s at the dosages of 0–15 g/kg chitosan but increased significantly to 216.1 mPa.s at 30 g/kg chitosan. Increase in viscosity indicates that the sludge suspension is more viscous and less flowable, which also means that the molecules are more strongly bound to each other as a result of chemical conditioning and thus less freely moveable (Ratkovich et al. 2013). The optimal dosage range of 15–20 g/kg chitosan has been identified in Section 5.3.1(c) because of the good dewaterability results indicated by low CST and supernatant turbidity, high cake solids content and near-zero zeta potential value. The low viscosity value obtained at 15 g/kg chitosan however revealed that the sludge flocs may be vulnerable to high shear and hence may not be susceptible to the subsequent high shear dewatering operation after chemical conditioning. The dosage of 20 g/kg chitosan seems to be a more favourable dosage with reasonably high structure resistance and high dewaterability.

The yield stress of suspensions is often linked to the existence of an interconnected three dimensional network of flocs and therefore the value of the yield stress may refer to the stress needed to overcome the cohesion Van-Der-Waals forces and cause the flow of the suspension (Seyssiecq et al. 2003). Table 6.3 shows that the yield stress increased from 0.34 Pa to 26 Pa which was two orders higher as the dosage of chitosan increased from 10 g/kg to 30 g/kg. This may be attributed to the increase in flocculated particle size as a result of increase in the energy of cohesion (when colloidal forces which tend to rebuild the structure overcome hydrodynamic forces which tend to maintain the solid structure broken) (Baudez 2008, Markis et al. 2014). The maximum yield stress obtained at the dosage of 30 g/kg correlated well with the highest floc size obtained at the same dosage (see Figure 5.7(f)). Yield stress can thus be applied as a useful indicator for the sludge's network strength to optimise chemical dosage in this study. Similar to the viscosity results, the dosage of 20 g/kg was selected as the optimal dosage rather than 15 g/kg due to its higher yield stress in correspondence with the optimum dewaterability results.

The rheograms obtained in this work were very similar to the ones studied by Wang and Dentel (2011) where they used AD sludge for conditioning experiments. They identified initial peak in their rheograms with peak values between 20–40 Pa at the polymer dosage of about 10–20 g/kg. Ayol et al. (2006) also used the similar peak stress value in flow curves and the network strength energy for the rheological evaluations and they found that the optimum polymer dose ranges identified from the peak values correlated well with those of CST results which indicated potentially useful relationship between rheological parameters and dewaterability. Table 6.3 shows that the peak values correlate well with the viscosity and yield stress values in response to the change of conditioner dosage. However fluctuations in the flow curve due to equipment sensitivity to flocculated suspension make it difficult to take the peak readings. Taking into account of both the sludge rheological properties and dewaterability, it can be concluded that the conditioning dosage of 20 g/kg was the most favourable dosage with its high-shear viscosity, yield stress and peak height in the rheogram recorded as 38.0 mPa.s, 7.40 Pa and 11.41 Pa respectively, in line with the low CST value of 6.6 s as shown in Figure 5.7(a).

6.3.3 Effect of other organic and inorganic chemical conditioning aids on sludge rheology

The rotational tests were conducted in suspended sludge medium for the effect of different organic polyelectrolytes and inorganic compounds as conditioning aids at a fixed dosage of 15 g/kg. Comparative rheograms of sludge conditioned with inorganic ferric chloride and organic chitosan are presented in Figure 6.9. Individual rheograms for each conditioner are given in Figures B.1–B.6 of Appendix B. The curves of the two conditioners in Figure 6.9 demonstrate a comparable trend where the inorganic experienced a higher magnitude of shear stress with increasing shear rate. The shear stress increased to a peak then gradually decreased until a steady state was reached, along with few smaller peaks in between. As discussed in Section 6.3.2, when shearing occurs, the flocculated sludge network structure would be stretched, broken and reformed, as indicated by the appearance of peaks in rheogram.

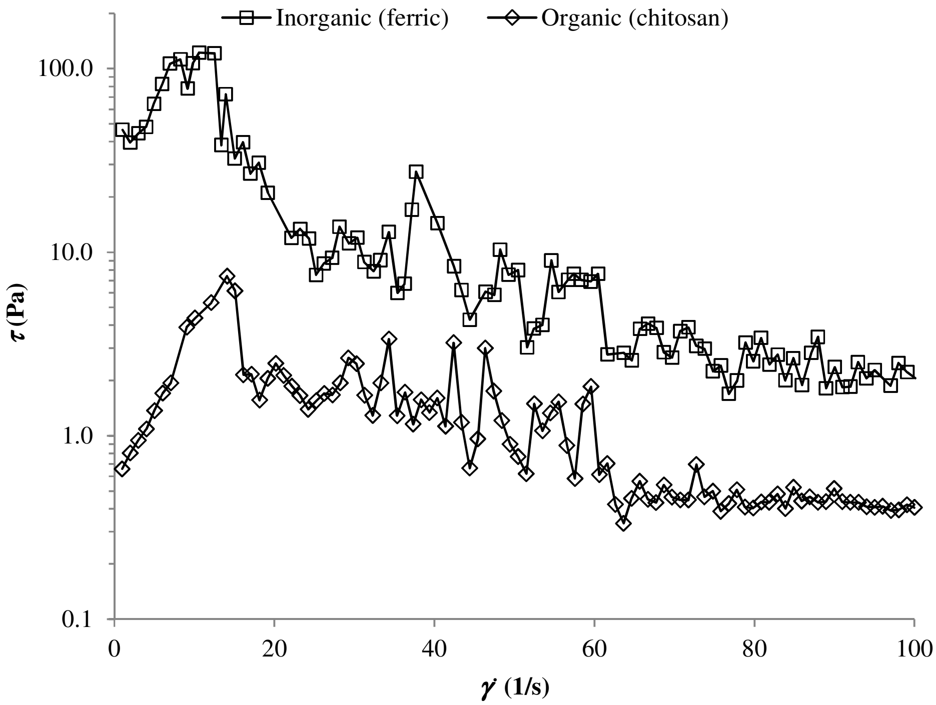


Figure 6.9 Rheograms of conditioned sludge with organic and inorganic conditioning aids at 15 g/kg

In this study, the trivalent aluminium and ferric cations (Al^{3+} and Fe^{3+}) exhibited very similar flow behaviour when subjected to the rotational test, with significantly higher network strength (measured by the rheological parameters) compared with the organic polyelectrolytes as shown in Table 6.4. The higher viscosity, yield stress and first peak height values obtained for Al^{3+} and Fe^{3+} were in agreement with the corresponding enhanced sludge dewaterability informed by the low CST values of 7.3–7.8 s (see Section 5.3.2, with CST results presented in Figure 6.10). The three organic polyelectrolytes, namely, the commercial polymer, EMA 8845, the polyacrylamide copolymer, PAC, and the cationic biopolymer, chitosan gave yield stress values which were two orders lower than the ones of inorganic conditioners. EMA 8845 and PAC showed moderately high peak values at low shear rates but the shear stress declined close to the one of chitosan at high shear rates (see supplementary Figures B.3–B.5 in Appendix B). The higher peak values may be attributed to the higher molecular weight of EMA 8845 and PAC with more cationic sites for binding and bridging to form larger floc structures.

Table 6.4 Rheological parameters obtained for different conditioning aids

Conditioner	High-shear viscosity[a] (mPa.s)	Yield stress[b] (Pa)	First peak height (Pa)
Ferric chloride	20.5	25.70	112.20
Aluminium chloride	15.6	19.24	89.04
EMA 8845	5.9	0.18	25.45
PAC	5.1	0.49	22.68
Chitosan	4.1	0.36	7.41
HCl (pH 2.3)	2.6	0.87	32.67

[a]High-shear viscosity was obtained at the shear rate of 100 s^{-1}.

[b]Yield stress was obtained by extrapolation at low shear rates.

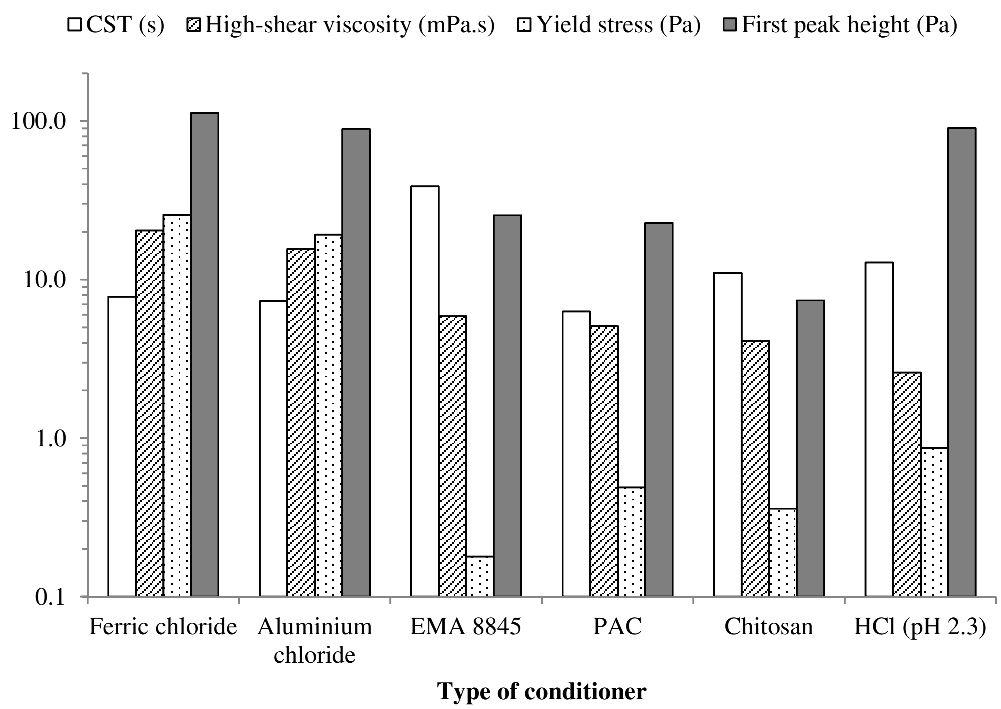


Figure 6.10 Comparative evaluation of sludge dewaterability (CST) and rheological parameters for different conditioning aids

According to Tadros (2010), as the shear rate increases, the floc structures may start to form layers that are coincident with the plane of shear, and this results in pseudoplastic flow. In the high-shear rate region, the layers can "slide" freely, and hence a pseudo-Newtonian region is obtained such as those in Figure 6.11, with a much lower viscosity that arises from purely hydrodynamic effect. From Table 6.4, it was found that the high-rate viscosities were about 4–6 mPa.s for the three organic polymers. As for the inorganic conditioners, the rigidity of the 3-D network structures formed from trivalent ion bridging together with the associated hydroxide precipitates may cause less "sliding" and hence higher viscosity than the organic conditioners as illustrated in Figure 6.11. The same explanation goes to the resulting higher yield stress and peak height for inorganic conditioners in Table 6.4.

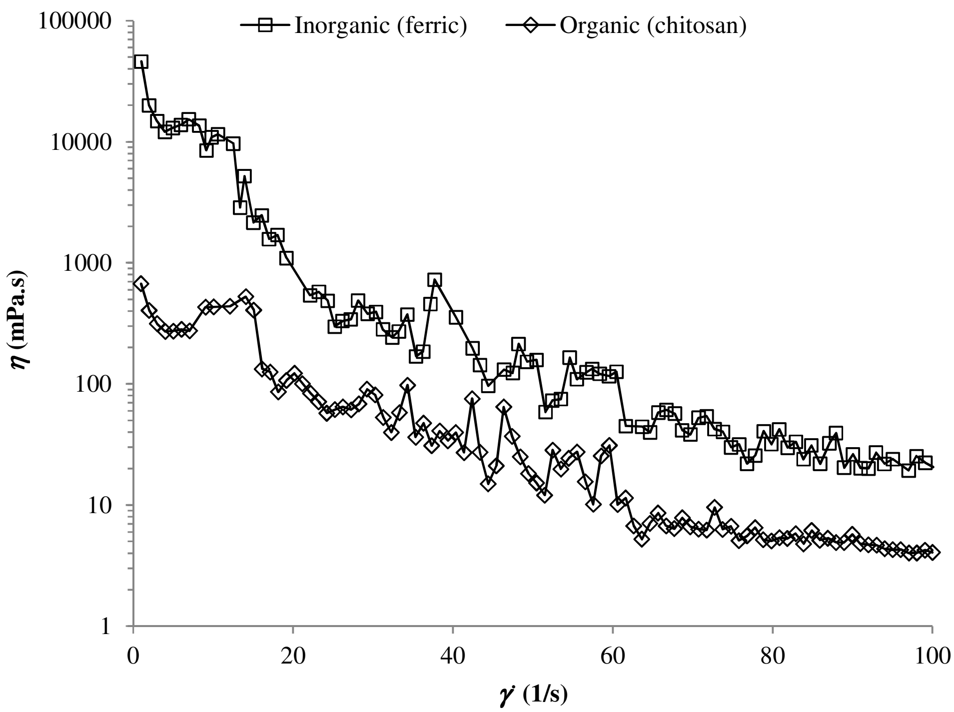


Figure 6.11 Viscosity-shear rate curves of conditioned sludge with organic and inorganic conditioning aids at 15 g/kg

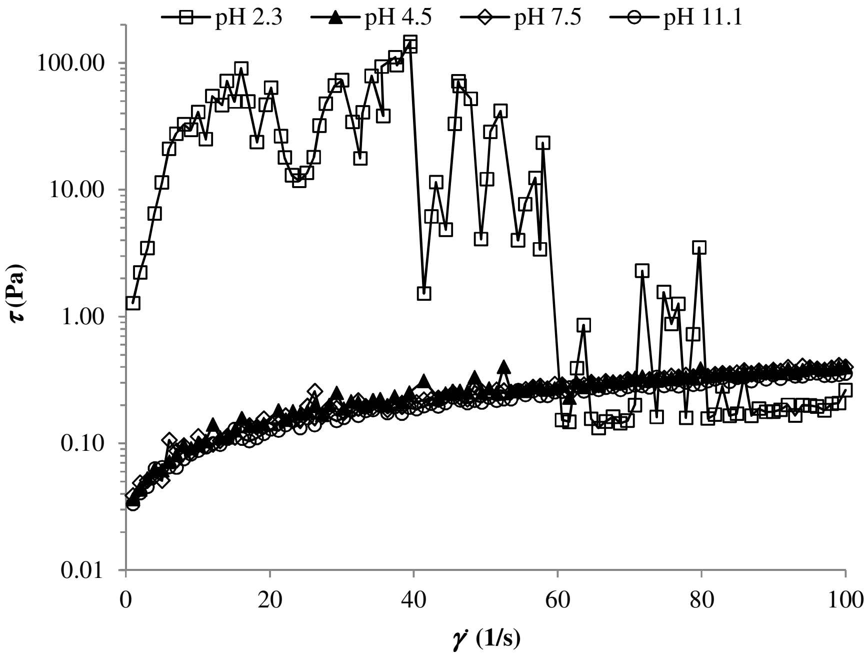
Treatment with inorganic acid, HCl, gave rather unpredictable flow properties to the sludge suspension. Higher peaks were observed in the rheogram (see supplementary Figure B.6) and the yield stress was relatively higher than the organic polymers, but the high-shear viscosity was the lowest among the few conditioners applied, as shown in Table 6.4. Details about acid and alkaline treatments and their effect on chitosan conditioning and sludge floc structures were discussed in Section 6.3.4. Although the organic polymers and the inorganic acid showed generally weaker network strength, the corresponding sludge dewaterability measured by CST was reasonably good, ranging from 6.3–12.8 s, except for EMA 8845 which recorded a CST value of 38.7 s, as illustrated in Figure 6.10.

6.3.4 Effect of conditioning pH on sludge rheology

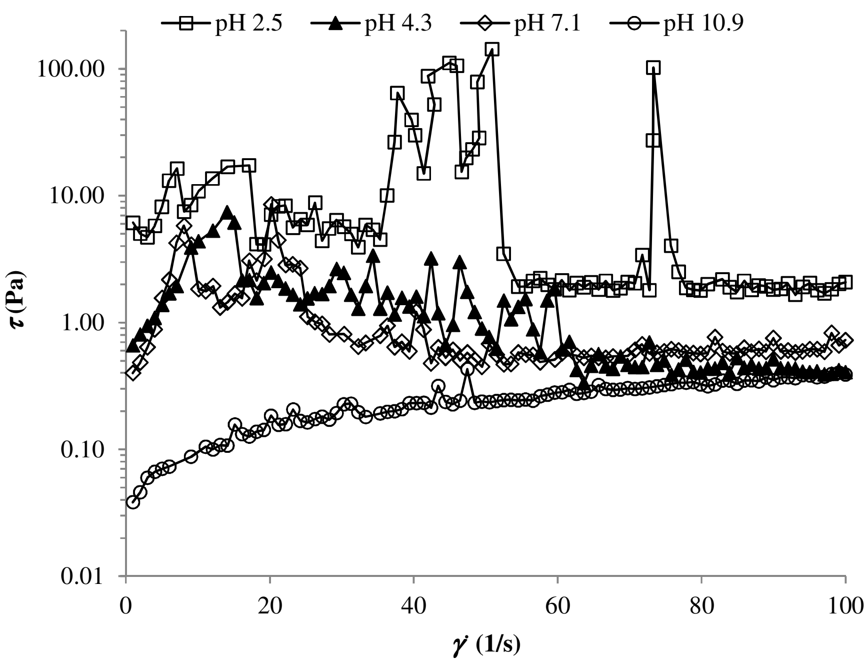
As discussed in Section 5.3.3, acid treatment (lowering pH) is more effective than alkaline treatment (increasing pH) as it may further enhance the ionisation of the amine groups of chitosan and suppresse the negative surface charges carried by the sludge particles. The rheograms in Figure 6.12(a) indicated that acid treatment alone significantly enhanced the sludge shear resistance to flow with a number of inconsistent peaks observed in the flow curve at pH 2.3. The presence of these peaks in the flow curve may arise from the presence of incoherent sludge ruptures as a result of acid treatment at pH 2.3. Sludge conditioned at other pHs did not show much difference in the flow behaviour where all can be modelled as power fluids, $\tau = K\dot{\gamma}^m$ with high confidence as given in Table 6.5.

Table 6.5 Best fit results of the power-law model for raw synthetic sludge under the effect of pH conditioning

pH	Consistency index, K (Pa.s^m)	Flow behaviour index, m	R^2
4.5	0.0288	0.5661	0.9710
7.5	0.0278	0.5671	0.9682
11.1	0.0242	0.5726	0.9810



(a) pH conditioning



(b) pH and polymer conditioning

Figure 6.12 Rheograms of (a) pH conditioned sludge and (b) pH–polymer conditioned sludge

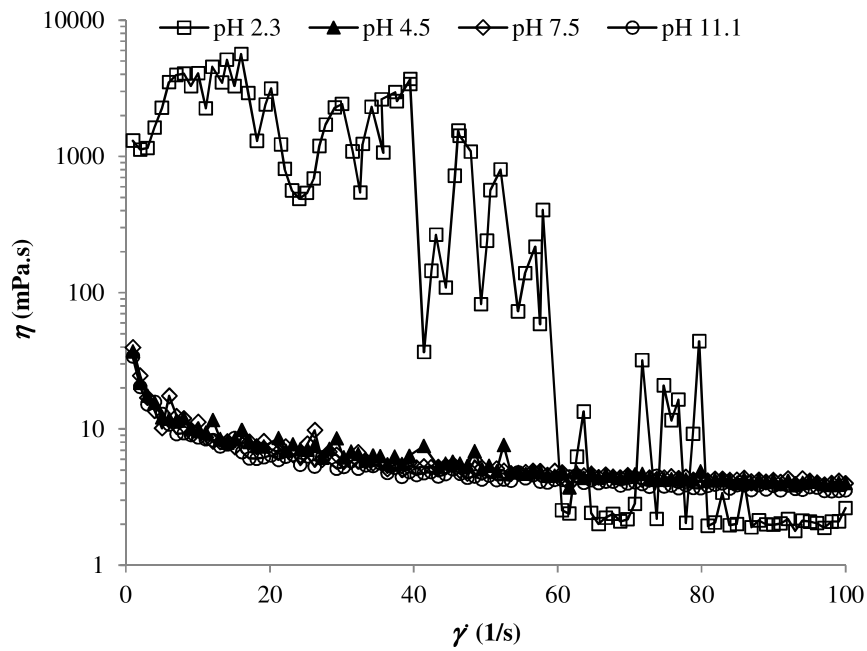
With a fixed dosage of chitosan polymer at 15 g/kg, increased shear resistance was observed for the pH–polymer conditioned sludge at pHs 2.5, 4.3 and 7.1 as presented in Figure 6.12(b). Unusual high peaks were observed at pH 2.5 at the mid-range of shear rates despite the initial peak. This may be attributed to the formation of the smaller and compactly bridged units of flocculated structures as a result of cell disruption and desorption of EPS from acid treatment combined with polymer bridging. The enhanced rheological properties at pH 2.5 as listed in Table 6.6 were in agreement with the dewaterability results in Section 5.3.3, indicating enhanced dewatering performance under acidic condition. Polymer conditioning at pH 10.9 did not enhance the sludge's network strength and the conditioned sludge retained its pseudoplastic flow behaviour with the corresponding lower sludge dewaterability. The viscosity-shear rate curves for the effect of conditioning pH are depicted in Figure 6.13. Similar trend of fluctuations were observed for the curves of the sludge conditioned at low pH without and with chitosan polymer.

Table 6.6 Rheological parameters obtained at different pHs with the conditioning dosage of 15 g/kg chitosan

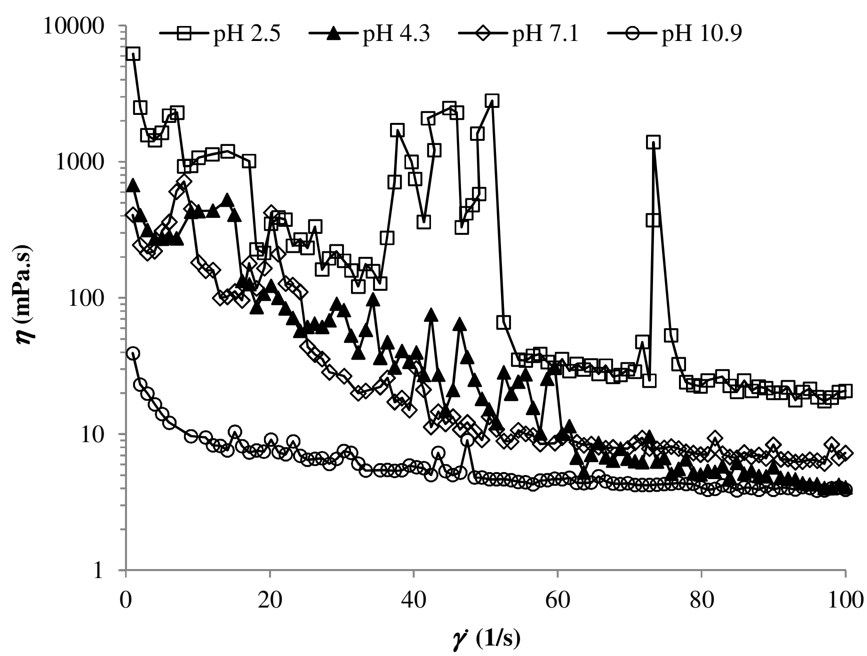
pH	High-shear viscosity[a] (mPa.s)	Yield stress[b] (Pa)	First peak height (Pa)
2.5	20.8	3.52	16.35
4.3	4.1	0.36	7.41
7.1	7.3	0.22	5.78
10.9	3.9	–	–

[a]High-shear viscosity was obtained at the shear rate of 100 s^{-1}.

[b]Yield stress was obtained by extrapolation at low shear rates.



(a) pH conditioning



(b) pH and polymer conditioning

Figure 6.13 Viscosity-shear rate curves of (a) pH conditioned sludge and (b) pH–polymer conditioned sludge

6.3.5 Effect of conditioning temperature on sludge rheology

Rheograms in Figure 6.14 show that the increase of temperature from 25°C to 35°C initially reduced the shear stress magnitude by two orders. As the temperature was increased further to 45–55°C, the shear stress reverted at a lower degree than the one at 25°C. The rheological properties at different conditioning temperatures were summarised in Table 6.7. It was also found that the increase in temperature from 25°C to 55°C resulted in decrease of yield stress from 4.16 Pa to 1.06 Pa based on the non-Newtonian Bingham model at low shear rates. The trend of a minimum point in the flow properties as a result of temperature increase was similar to the change of CST results in Section 5.3.4 where a minimum CST value of 4.7 s was found at 35°C.

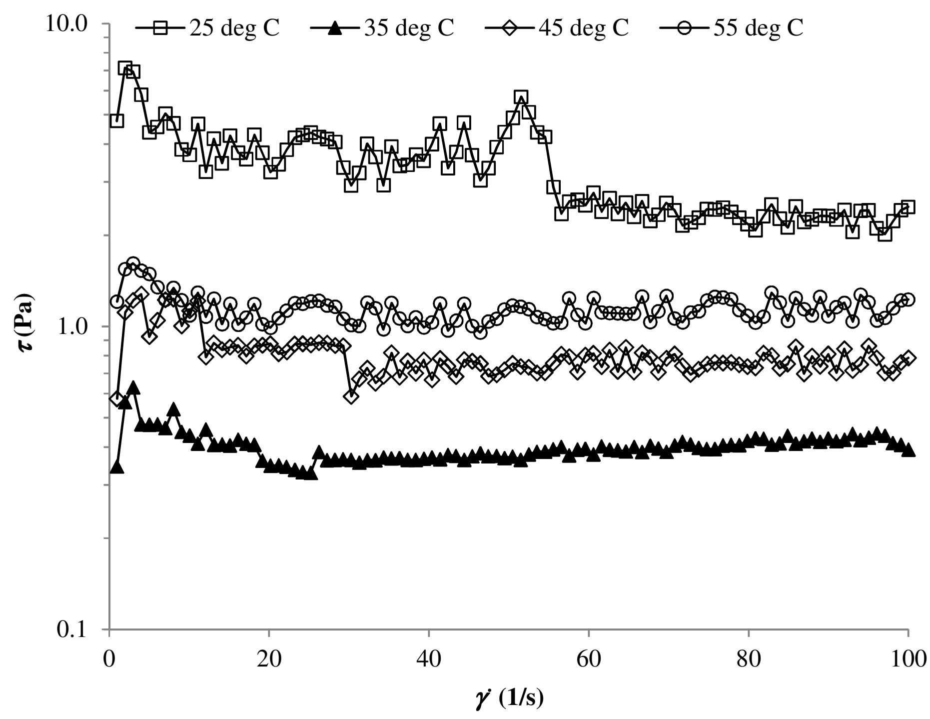


Figure 6.14 Rheograms of conditioned sludge at different temperatures

Table 6.7 Rheological parameters obtained at different temperatures with the conditioning dosage of 20 g/kg chitosan

Temperature (°C)	High-shear viscosity[a] (mPa.s)	Yield stress[b] (Pa)	First peak height (Pa)
25	24.8	4.16	7.13
35	3.9	0.23	0.63
45	7.9	0.34	1.28
55	12.3	1.06	1.61

[a]High-shear viscosity was obtained at the shear rate of 100 s^{-1}.

[b]Yield stress was obtained by extrapolation at low shear rates.

The viscosity generally showed reduction with increasing temperature and shear rate as shown in Figure 6.14. It is well known that increase in temperature will cause a decrease in sludge viscosity according to the Arrhenius type equation (Eshtiaghi et al. 2013):

$$\eta_\infty = K \exp\left(\frac{E_a}{RT}\right) \tag{6.1}$$

where η_∞ is limit viscosity, K the empirical constant, T the absolute temperature, R the universal gas constant, and E_a the activation energy. This may explain the initial decrease in viscosity when the sludge was mildly heated at 35°C. Further thermal heating may cause enhanced solubilisation of EPS and cell disruption where the intracellular materials are released to the bulk solution and interfere with the rheological behaviour of the conditioned sludge along with change in shape and size of flocculated particles. Baudez et al. (2013) pointed out that the presence of dissolve compound converted from AD sludge solids as a result of temperature increase might cause change in sludge structure and composition. They believed that the usual expression to model temperature dependence of sludge is not applicable due to change in sludge composition as it would be fundamentally inaccurate to consider constant activation energies under this condition. Similarly in the present study, the release of intracellular materials with increasing thermal treatment has altered the sludge network with increased viscosity and yield stress but reduced dewaterability as explained in Section 5.3.4.

Another interesting point to note from the rheograms is that the ruptures of sludge network caused by heating somehow result in more consistent flow curves and viscosity-shear rate curves as shown in Figures 6.14 and 6.15. No significant peaks were observed in these plots for the range of 35–55°C indicating a reduction in the inhomogeneity of the flocculated sludge structures. The impact of temperature on the rheological behaviour of conditioned sludge has not been studied considerably elsewhere. The findings from this study have attempted to relate the sludge rheology and dewaterability with the change of sludge network structure as a result of temperature increase for the mesophilic (35–37°C) and thermophilic (45–60°C) regions.

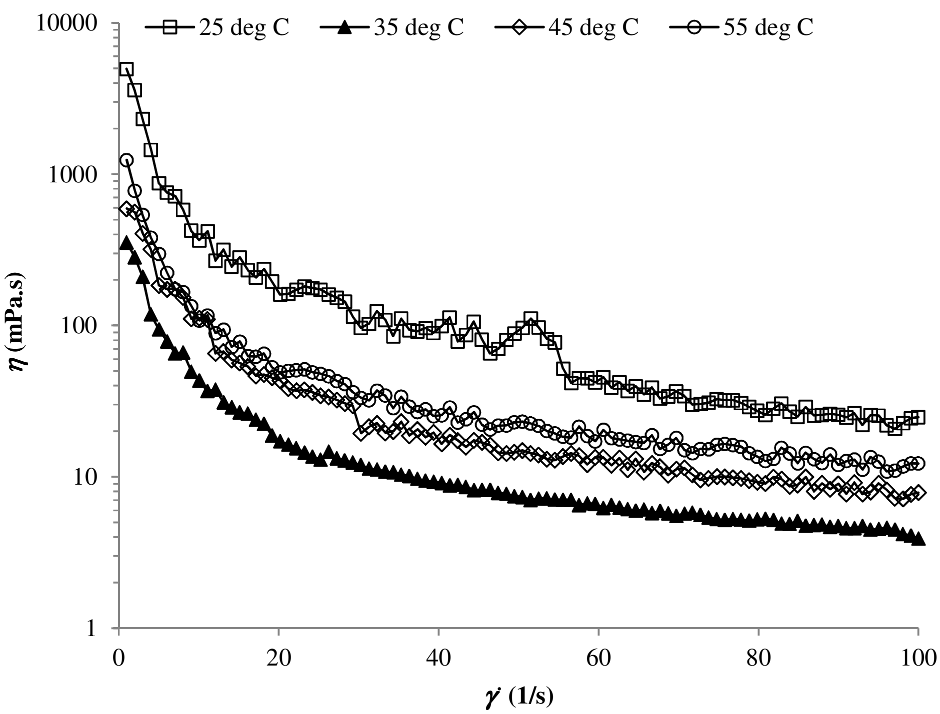


Figure 6.15 Viscosity-shear rate curves of conditioned sludge at different temperatures

6.3.6 Effects of mixing speed and mixing time during flocculation

Figure 6.16 shows the selected rheograms of conditioned sludge at low and high mixing speeds during flocculation. The rheogram of conditioned sludge at the mid mixing speed of 150 rpm is given in the supplementary Figure B.7. From the rheological data given in Table 6.8, increase in mixing speed to 300 rpm somehow weakened the rheological strength of the conditioned sludge. Increased mixing intensity may destroy the sludge structure exposing more negatively charged surfaces and cause deterioration in sludge dewaterability as found in Section 5.3.5. A lower degree of mixing is always favoured in the flocculation step for sufficient particle contact without excessive shearing. The rheological results suggested that slow mixing at 50 rpm promoted the buildup of sludge network strength and enhanced dewaterability at the same time. The viscosity-shear rate curves for the effect of mixing speed are presented in the supplementary Figure B.8.

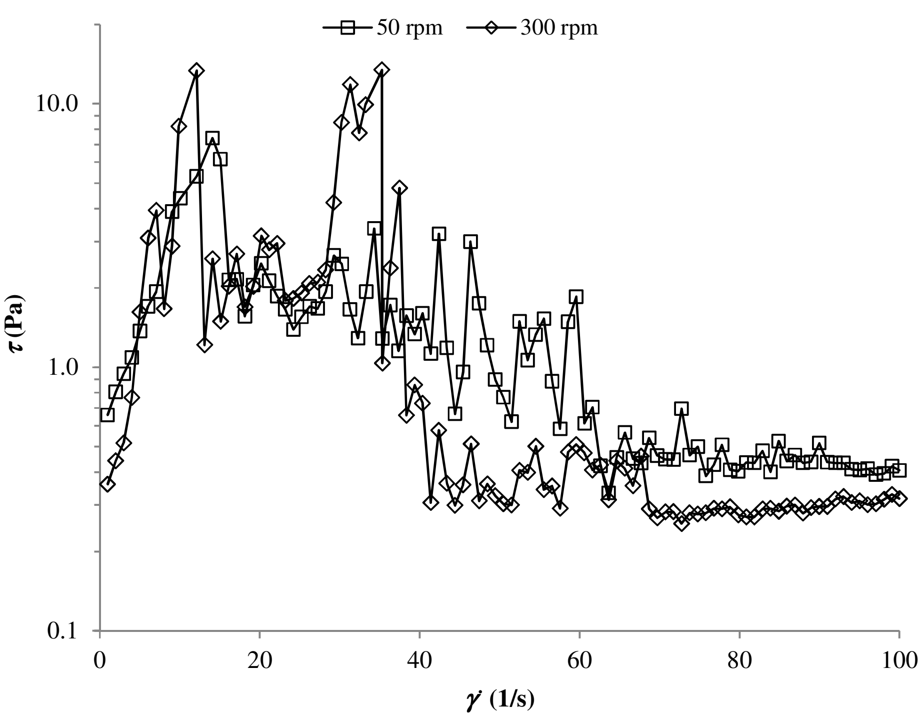


Figure 6.16 Rheograms of conditioned sludge at different mixing speeds

Table 6.8 Rheological parameters obtained at different mixing speeds with the conditioning dosage of 15 g/kg chitosan

Mixing speed (rpm)	High-shear viscosity[a] (mPa.s)	Yield stress[b] (Pa)	First peak height (Pa)
50	4.1	0.36	7.41
150	3.1	1.10	1.50
300	3.2	0.28	3.94

[a]High-shear viscosity was obtained at the shear rate of 100 s^{-1}.

[b]Yield stress was obtained by simple extrapolation at low shear rates.

The effect of mixing time on the rheological behaviour of conditioned sludge was presented in Figure 6.17. The rheogram of conditioned sludge without mixing during the flocculation step (mixing time = 0 s) is given in the supplementary Figure B.9. The results revealed that 60 s mixing was enough to flocculate the sludge with good network strength as indicated by the viscosity and yield stress in Table 6.9. Increase in mixing time for the flocculation step gave less impact to the sludge dewaterability as mentioned in Section 5.3.5. Likewise, the change in rheological data was less significant for the ranges of mixing speed and mixing time applied. The viscosity-shear rate curves for the effect of mixing time are presented in the supplementary Figure B.10.

Table 6.9 Rheological parameters obtained at different mixing times with the conditioning dosage of 15 g/kg chitosan

Mixing time (s)	High-shear viscosity[a] (mPa.s)	Yield stress[b] (Pa)	First peak height (Pa)
0	6.3	1.41	5.86
60	11.4	2.69	5.22
300	4.1	0.36	7.41

[a]High-shear viscosity was obtained at the shear rate of 100 s^{-1}.

[b]Yield stress was obtained by simple extrapolation at low shear rates.

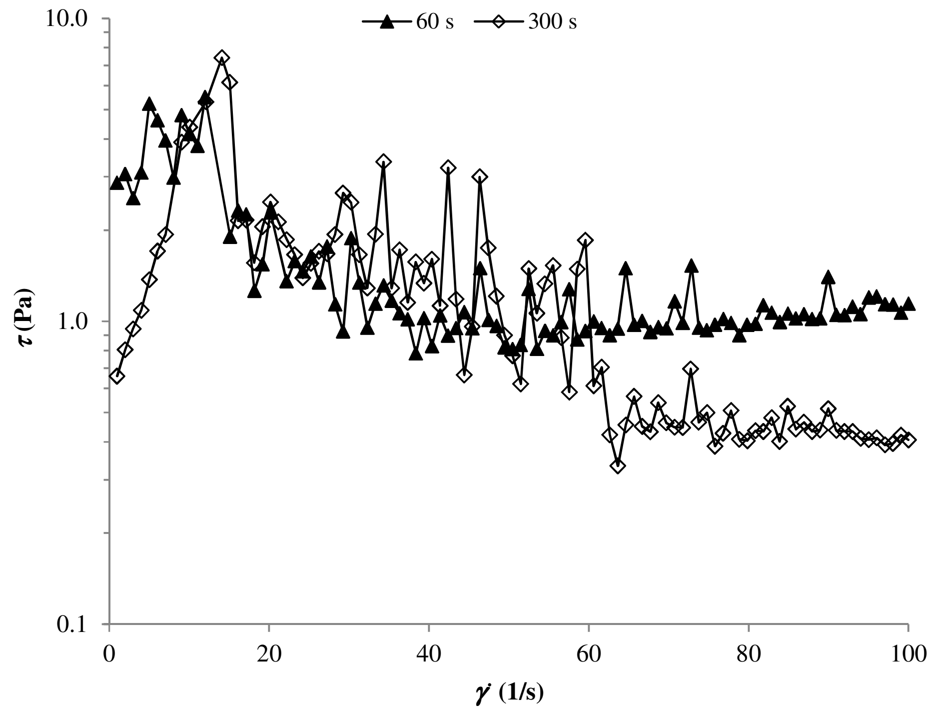


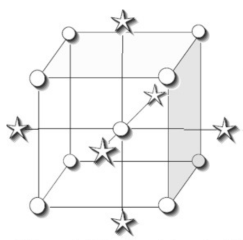
Figure 6.17 Rheograms of conditioned sludge at different mixing times

6.3.7 Optimisation of controlling process parameters using rheological and dewaterability parameters

Combining the results from both rheological and dewaterability studies, three controlling process parameters or factors were selected for the optimisation of the sludge conditioning process, namely chemical dosage, pH and temperature. The process was explored using the most popular response surface method (RSM) design, called central composite design (CCD), with the help of Design-Expert 9 software. In general, RSM aims to attain the optimal process settings to achieve the best performance.

(a) CCD response surface design background

CCD is well suited for fitting a quadratic surface in process optimisation and is insensitive to missing data. It is created from a 2-level factorial design, augmented with centre points and axial points (as shown in Figure 6.18). The optimisation was aided with the performance responses from rheological and dewaterability parameters identified earlier. The factor levels were decided based on the previous results. A standard RSM design by CCD consists of twenty experimental runs with eight factorial points, six axial (star) points and six centre points. The current study however used a reduced RSM design with two centre points instead of six. Table 6.10 shows the design summary results imported from the software.



Factor	Unit	Factorial		Axial (Star)[a]	Centre
		Low Level (–1)	High Level (+1)		
A: Dosage	g/kg	10.0	20.0	6.6–23.4	15.0
B: pH		4.0	9.0	2.3–10.7	6.5
C: Temperature	°C	35.0	55.0	28.2–61.8	45.0

[a]The axial (star) points set at 1.68179 coded units from the centre–a conventional choice for the CCD (Design-Expert 9 User's Guide), which fit reasonably within the factor ranges for this study.

Figure 6.18 Central composite design for three factors in response surface study

(b) CCD response surface analysis

Responses from each type of measurement were modelled as a function of the factors varied in the RSM experiments. According to Design-Expert 9 User's Guide (2013), the software allowed the responses to be analysed using "sequential model sum of squares", which indicated how terms of increasing complexity from linear model to cubic model contributed to the total model. The sum of squares was computed by squaring the mean of all response values and multiplying it by the number of runs (Anderson and Whitcomb 2005). For each source of terms (linear, etc.), the software examined the probability ("Prob > F") to see if it fell below 0.05 (a conventional statistical significance level) and suggested the most adequate model. The provisional model was tested for Lack of Fit which compared residual error with pure error from replicated design points. For insignificant lack of fit, the probability value (“Prob > F”) must be greater than 0.1 for a satisfactory model. For this study, the linear model turned out to be the most adequate model based on the final assessment of the maximum adjusted and predicted R^2, and the minimum predicted residual sum of squares (PRESS).

Table 6.10 Design summary generated from Design-Expert software with response data from experiments

		Factor 1	Factor 2	Factor 3	Response 1	Response 2	Response 3	Response 4
Std	Space Type	A:Dosage	B:pH	C:Temperature	CST	Viscosity	Yield stress	Peak height
		g/kg		°C	s	mPa.s	Pa	Pa
1	Factorial	10.0	4.0	35.0	10.4	5.6	1.19	1.51
2	Factorial	20.0	4.0	35.0	4.7	3.9	0.23	0.63
3	Factorial	10.0	9.0	35.0	68.3	4.2	0.26	0.54
4	Factorial	20.0	9.0	35.0	38.7	4.8	0.60	1.05
5	Factorial	10.0	4.0	55.0	13.1	6.8	0.61	0.79
6	Factorial	20.0	4.0	55.0	6.3	12.3	1.06	1.61
7	Factorial	10.0	9.0	55.0	75.7	2.5	0.10	0.25
8	Factorial	20.0	9.0	55.0	22.1	6.2	0.79	1.53
9	Axial	6.6	6.5	45.0	30.2	12.7	0.50	1.10
10	Axial	23.4	6.5	45.0	5.0	159.3	19.35	20.88*
11	Axial	15.0	2.3	45.0	5.4	2427.0	196.08	388.10*
12	Axial	15.0	10.7	45.0	49.4	9.8	0.33	0.53
13	Axial	15.0	6.5	28.2	5.9	9.3	2.82	4.12
14	Axial	15.0	6.5	61.8	10.5	5.2	0.57	0.82
15	Center	15.0	6.5	45.0	7.4	29.0	3.25	4.16
16	Center	15.0	6.5	45.0	6.1	30.1	3.20	4.54

* Outliers

The selected model was inspected by the analysis of variance (ANOVA) as given in Table 6.11. The model F-value of 22.05 implied the model was significant where there was only a 0.01% chance that an F-value this large could occur due to noise. The two factors, dosage and pH, were identified as the significant terms in the model with values of "Prob > F" less than 0.05. The effect of temperature was insignificant and was hence removed to improve the model. The "Lack of Fit F-value" of 6.33 implied the Lack of Fit was not significant relative to the pure error. There was a 30.19% chance that a ""Lack of Fit F-value"" this large could occur due to noise. The reduced model exhibited a reasonable agreement between the adjusted and predicted R^2, and the signal to noise ratio of 11.711 (measured by Adequate Precision "Adeq Precision") indicated an adequate signal.

Table 6.11 ANOVA for data from CCD on sludge dewaterability

ANOVA for Response Surface Reduced Linear model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.18	2	0.091	22.05	< 0.0001	significant
A-Dosage	*0.054*	*1*	*0.054*	*13.06*	*0.0031*	
B-pH	*0.13*	*1*	*0.13*	*31.04*	*< 0.0001*	
Residual	0.054	13	4.117E-003			
Lack of Fit	*0.053*	*12*	*4.402E-003*	*6.33*	*0.3019*	*not significant*
Pure Error	*6.949E-004*	*1*	*6.949E-004*			
Cor Total	0.24	15				

Std. Dev.	0.064	R-Squared	0.7723
Mean	0.30	Adj R-Squared	0.7373
C.V. %	21.61	Pred R-Squared	0.6913
PRESS	0.073	Adeq Precision	11.711

According to the reduced model, the final equation in terms of coded factors was found as:

$$\frac{1}{\sqrt{CST}} = 0.30 + 0.063A - 0.097B \tag{6.2}$$

where *A* refers to the chemical dosage and *B* the pH.

On the other hand, the final equation in terms of actual factors was given as:

$$\frac{1}{\sqrt{CST}} = 0.36015 + 0.012549\,Dosage - 0.038694\,pH \tag{6.3}$$

The coded equation was useful for identifying the relative impact of the factors by comparing the factor coefficients. In this case, Equation 6.2 suggests that the impact of pH is more significant than the one of chemical dosage. Meanwhile Equation 6.3 in terms of actual factors can be used to make predictions about the response for given levels of each factor but the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor. For example, for the dosage of 15 g/kg chitosan at pH 7, the predicted CST value from Equation 6.3 is 13.0 s (compared to the actual CST value of 11.8 s).

Before the response surfaces were generated from the model, the residuals were diagnosed for abnormalities as prompted by the software. The diagnostic details provided by Design-Expert 9 were given in several plots via the Diagnostics tab, as shown in Figure 6.16, with the purposes explained by Design-Expert 9 User's Guide (2013):

1) Normal probability plot of the studentized residuals to check for normality of residuals (in which case the points will follow a straight line)
2) Studentized residuals versus predicted values to check for constant error (where the plot should be a random scatter)
3) Externally Studentized Residuals to look for outliers, i.e., influential values (it helps to detect a value, or group of values, that are not easily predicted by the model)

4) Box-Cox plot for power transformations (provides a guideline for selecting the correct power law transformation, based on the best lambda value, which is found at the minimum point of the curve generated by the natural log of the sum of squares of the residuals)

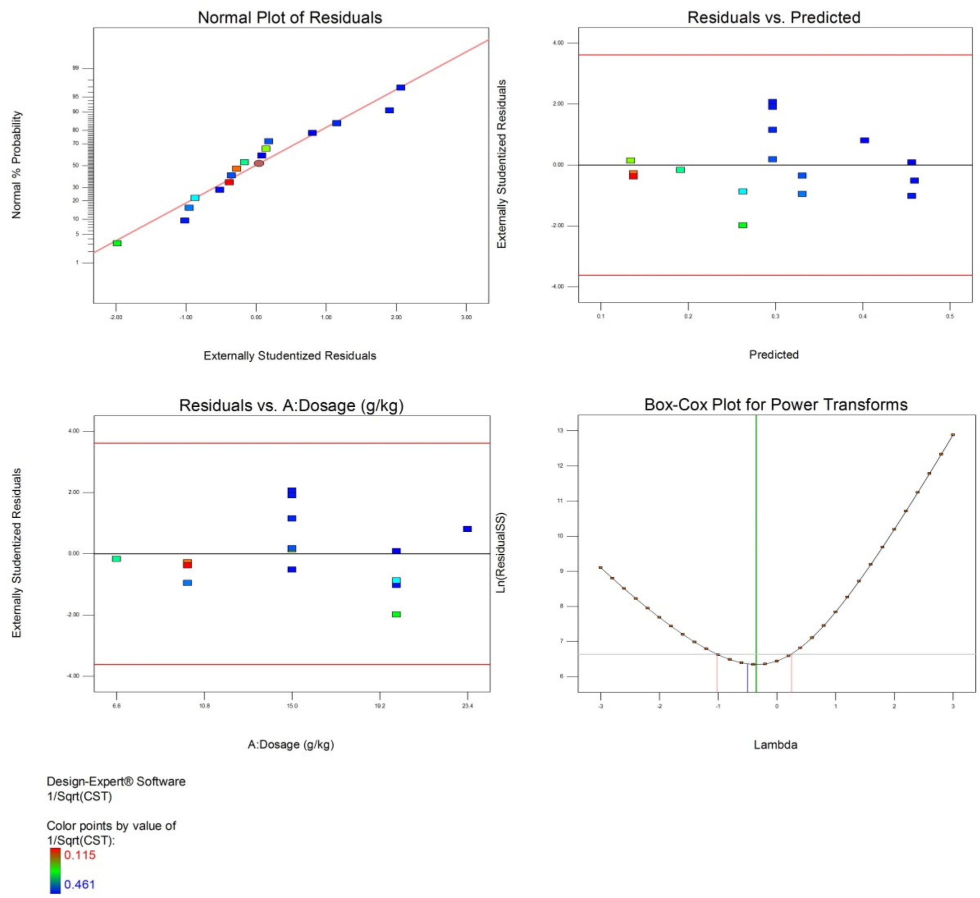
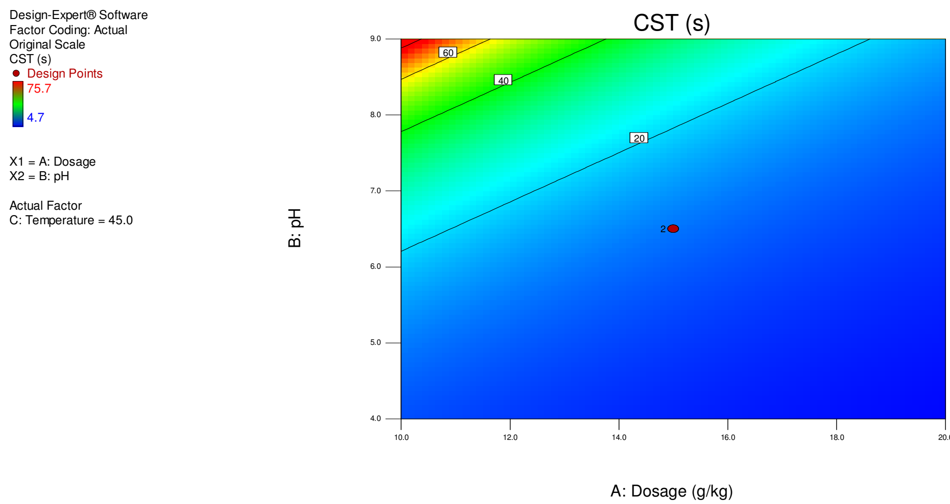


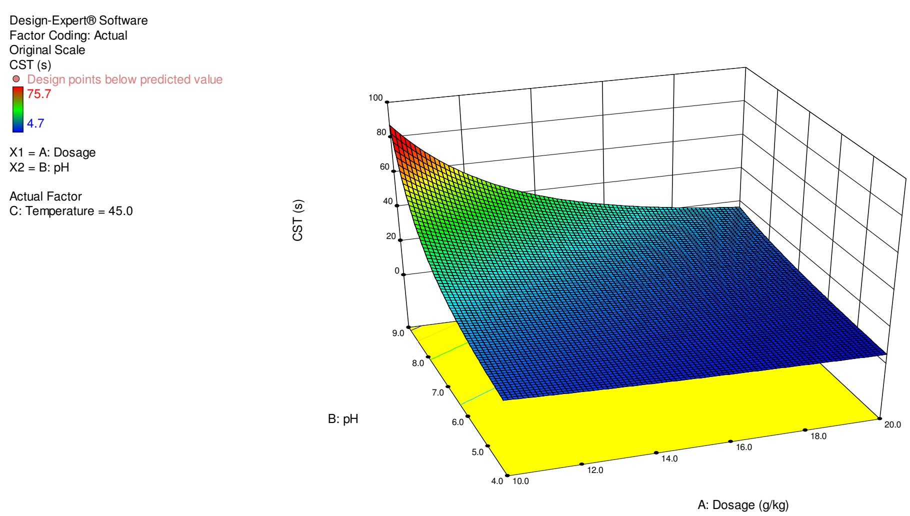
Figure 6.19 Diagnostic plots generated by Design-Expert

From Figure 6.19, the normal plot of residuals lined up nicely as expected from a normal distribution, which means the residuals are pure noise and contain no signal. The other plots exhibited a reasonable random scatter after a recommended transformation of inverse square root from the Box-Cox plot. The residuals diagnosis revealed no statistical problems for the predicted model.

A contour plot and 3D plot of the predicted response as a function of dosage and pH were produced in Figure 6.20 with the factors held within their factorial range. By inspection of graphs (and verified by numerical optimisation), the peak dewaterability can be found at the dosage of 20 g/kg and pH 4 with the predicted CST value of 5.1 s, which was close to the actual CST value of 5.3 s from a follow-up run of confirmation.



(a)



(b)

Figure 6.20 Model graphs in the form of (a) a contour plot and (b) a 3D plot

Despite the two outliers as shown in Table 6.10, no significant models were identified for the rheological responses measured by the high-shear viscosity, yield stress and first peak height. The unusually high rheological values were found at the axial points with the lowest pH of 2.3 and the outermost dosage of 23.4 g/kg as compared to the factorial range.

6.4 Conclusion

Sludge suspensions are always non-Newtonian fluids. The apparent viscosity of such materials is a function of the shear rate. The determination of non-Newtonian rheological properties of such fluid cannot be related to a single value of its viscosity. It is linked to the determination of the whole rheogram. The findings from this study revealed that at least two common rheological models can be used to describe the sludge rheology under different physicochemical and operating conditions in the conditioning process. The raw or unconditioned synthetic sludge exhibited shear thinning behaviour that followed the power-law model, $\tau = K\dot{\gamma}^{m}$ regardless of the sampling location. When conditioned with chitosan, only sludge sampled from the fluid phase exhibited an excellent fit of the Bingham model, $\tau = \tau_0 + \eta\dot{\gamma}$ over the range of shear rate up to 100 s^{-1}. The flow properties of suspended sludge and settled sludge after conditioning were difficult to model with the commonly known sludge models over the range of applied shear rate as the polymer-sludge network strength was disrupted and broken into smaller units of flocculated spheres under shear.

The results from the rheological analysis are listed as follows:

- Increase in conditioner dosage enhanced sludge resistance to flow and network strength as indicated by the increase in viscosity, yield stress and peak height in the rheogram. The dosage of 20 g/kg was selected as the optimal dosage rather than 15 g/kg due to the improved rheological behaviour in reasonable agreement with the optimum dewaterability results.
- Inorganic chemicals exhibited favourable network strength of one to two orders higher than the ones of organic chemicals.
- Acid treatment significantly enhanced the sludge shear resistance to flow. Unusual high peaks were observed in the rheogram of sludge conditioned at

pH 2.5 at the mid-range of shear rates possibly due to the formation of the smaller and compactly bridged units of flocculated structures from acid treatment combined with polymer bridging.

- The change in rheological data was less significant for the ranges of mixing speed and mixing time applied in this study, similar to the corresponding sludge dewaterability results.
- The rheological properties correlated well to the sludge dewaterability parameter under the different physicochemical and operating parameters. Change in temperature gave more impact to sludge rheology compared to sludge dewaterability.
- Rheology can be used as a tool to optimise the chemical dosage in sludge conditioning and dewatering when used in conjunction with sludge dewaterability parameter. Both high-shear viscosity and yield stress can be applied as a useful indicator for the sludge's network strength to optimise chemical dosage. Rheogram peak value can be a potential marker but special care is required in taking the peak readings when there are significant fluctuations or low signal to noise ratio in the flow curve.
- The RSM design was able to model the sludge dewaterability measured by CST as a function of chemical dosage and pH. The change in pH gave more impact to sludge dewaterability compared to the dosage effect. The effect of temperature was found insignificant. The optimal process settings were predicted at the dosage of 20 g/kg and pH 4 within the factorial range applied. The RSM was not able to model the rheological behaviour in this study.

References

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CHAPTER 7

APPLICATION OF SINGLE AND DUAL-CONDITIONING AIDS ON ANAEROBIC DIGESTED SLUDGE AND SEPTIC SLUDGE*

7.1 Introduction

This chapter introduces the application of chitosan polymer in both anaerobic digested (AD) sludge and septic sludge, and presents the comparative evaluation of single and dual-conditioning aids to improve sludge dewaterability. When used in conjunction with organic polymer such as chitosan in dual conditioning, inorganic metal cations may have significant effects on the coagulation and flocculation of the treated sludge by additional neutralisation of negative surface charges, ion-bridging of floc components, and salting out effect, leading to improved dewaterability. Hence dual-chemical conditioning and dewatering may become an effective and attractive conditioning method through cost effective selection of combined organic and inorganic chemicals. This study presents the potential of dual-conditioning using the nontoxic and biodegradable chitosan polymer to replace the conventional synthetic polymers, together with some cheaper inorganic metal cations such as ferric chloride as an economical and eco-friendly sludge dewatering alternative. The optimum conditioning doses and dual-chemical combinations were also determined in the study.

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7.2 Materials and Methods

The application of single and dual-conditioning aids was evaluated in both AD sludge and septic sludge for comparison. The AD sludge characteristics were presented and discussed in Section 4.3.1. The septic sludge samples were supplied by Kiara Bumimas Sdn. Bhd., a local desludging contractor in Miri, Sarawak, Malaysia. The sludge characteristics were determined using Standard Methods 2540 for total solids (TS), as well as Standard Methods 2710 for capillary suction time (CST) according to APHA (2012). Total dissolved solids (TDS), pH and temperature were measured using bench meters. The specific resistance to filtration (SRF) test was conducted using a simple laboratory filtration system as described in Section 3.4.2. Moisture content was determined by taking the weight of the filtered sludge cake before and after drying in an oven at 103–105°C overnight. The septic sludge characteristics are presented in Table 7.1.

Table 7.1 Characteristics of septic sludge

Property	Septic sludge
Total solids (TS), g/L	*23.2*
Total dissolved solids (TDS), g/L	*0.6*
Capillary suction time (CST), s	*93.9*
pH	*7.55*
Specific resistance to filtration (SRF), m/kg	1.52×10^{14}
Filtered cake solids content, %	*10.3*

Some changes were made to the materials available and mixing conditions for septic sludge. The conditioning biopolymers used were low molecular weight (MW) chitosan (50,000-190,000 Da, Aldrich) and medium MW chitosan (600,000-800,000 Da, Acros Organics). They were prepared as 0.5% stock solutions by dissolving 0.5 g chitosan in 100 mL of 1% acetic acid solution. The inorganic conditioners used were laboratory grade chloride salts of sodium, potassium, magnesium, calcium, aluminium, and ferric (trivalent) iron. They were prepared as 1.0% stock solutions.

The conditioning experiments were performed as per method published in Lau et al. (2015) which was described in detail in Section 3.3. The experiments were conducted with rapid mixing at 500 rpm for 2 minutes and subsequently slow mixing at 200 rpm for 5 minutes, to study both the single conditioning and dual-conditioning effects. The dewatering performance of the conditioned sludge was assessed immediately after mixing for the CST and filtered sludge cake solids content. The SRF was evaluated together as a dewaterability parameter in this case.

7.3 Results and Discussion

7.3.1 Effect of molecular weight and dosage of polymer in single conditioning of septic sludge

The relationship between the MW and dosage of chitosan polymer in the septic sludge conditioning process is presented in Figure 7.1. It can be seen that the medium MW chitosan showed greater reduction in CST at dosages between 2.5 and 10 g/kg than the low MW chitosan (see Figure 7.1(a)). At dosages between 15 and 20 g/kg, there was no significant difference in CST reduction as both the polymers reached plateaus at an average CST of about 28 s. The SRF results also supported those of CST and showed a decreasing trend until they levelled off at a dosage of 20 g/kg as shown in Figure 7.1(b). The conditioning results with septic sludge exhibited similar decreasing trend with increase in polymer dosage such as those of AD sludge and synthetic sludge which are presented in Section 5.3.1(a).

Investigation of the solids content of the filtered sludge cake reveals that varying the conditioner dose seemed to have little effect once it reached an average of about 26% for both the chitosan polymers as shown in Figure 7.1(c). Before conditioning and dewatering, the solids content of the raw sludge was only 2.3%, which indicates poor sludge dewaterability with high moisture content. After filtration dewatering, the solids content of unconditioned sludge had increased to 10.3%. With polymer conditioning, the cake solids content increased significantly further to about 26% for both the chitosans. Increase in the polymer dosage increased the dewatering rate (or the filterability of sludge), as indicated by the CST and SRF results but did not further enhance the filtered sludge cake contents after the dosage of 2.5 g/kg.

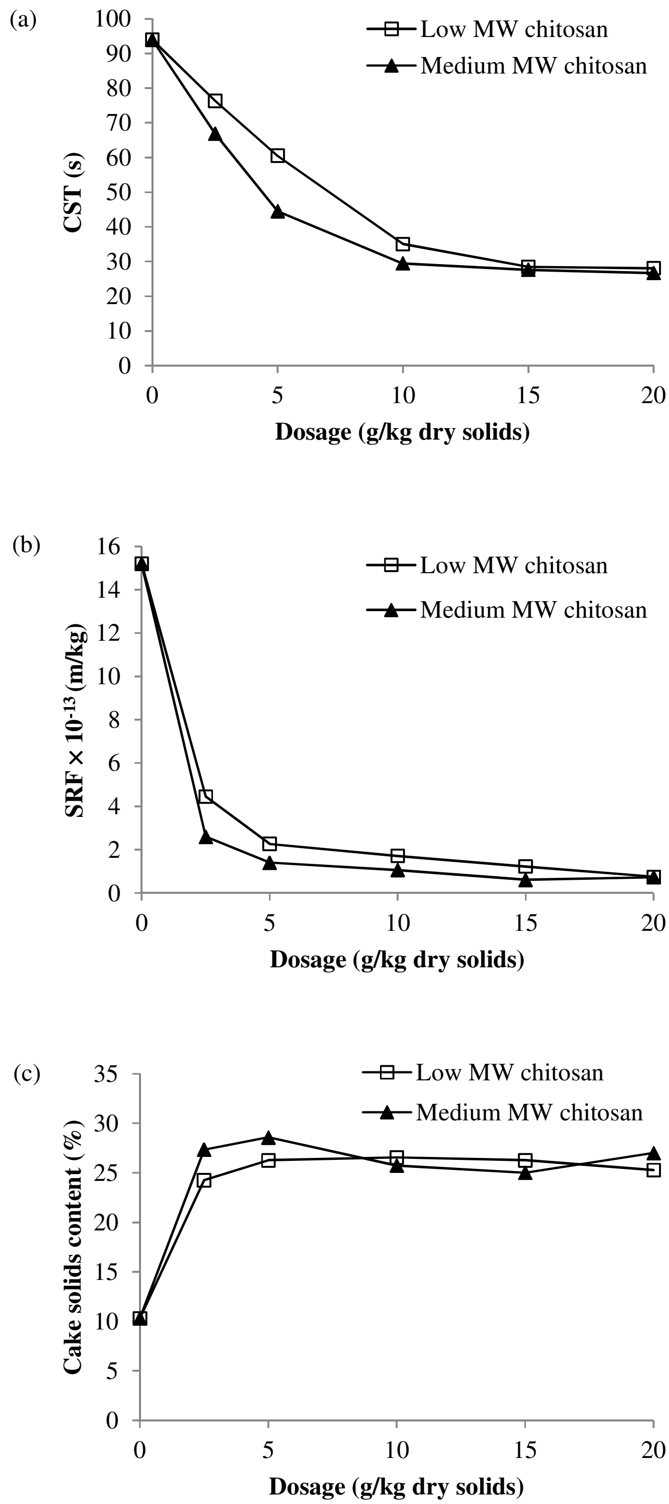


Figure 7.1 Effect of chitosan dosage on sludge dewaterability expressed in terms of (a) CST, (b) SRF, and (c) filtered cake solids content

As explained in Section 5.3.1(a), increase in MW of a cationic polymer introduces more cationic sites as a result of its longer chains, which may improve sludge flocculation and dewatering. Hence a lower dosage of the medium MW chitosan can achieve higher dewaterability than the low MW chitosan used in this study. The same was observed for AD sludge in Section 5.3.1(a). Once all negatively charged sludge surfaces were presumably occupied and polymer bridging took place, increasing polymer dosage yielded no further improvement in sludge dewaterability as depicted in Figure 7.1. The results suggest that the range of 15–20 g/kg chitosan was the optimum chemical dosage for both the chitosans applied in the present study. Restabilisation did not occur within the range of polymer dosage applied as there was no deterioration in dewaterability. These findings are consistent with the previous studies using AD sludge and synthetic sludge in Section 5.3.1(b).

7.3.2 Effect of dual-conditioning in enhancing sludge dewatering

(a) Dual-conditioning in septic sludge

A fixed dose of 5 g/kg chitosan was selected for studying the dual-conditioning method with different species of inorganic metal cation in the septic sludge system. It represents approximately one third to a quarter of the optimum dose range, effective for about 35–55 % CST reduction for the low and medium MW chitosans, based on the results in Section 7.3.1. The aim was to assess the possibility of using the less expensive metal cation to supplement chitosan in sludge conditioning, to achieve a similar level of dewaterability.

Table 7.2 shows the changes in sludge dewaterability produced by different types and combinations of conditioners. Dual-conditioning of sludge using chitosan and metal cations contributed significantly to CST and SRF reductions in comparison with the single use of either chitosan or metal cation(s). The enhanced dual-conditioning effect was more noticeable for monovalent and divalent cations compared to trivalent cations. The effect of MW became less when chitosan was used in conjunction with cations. Nevertheless, dual-conditioning using a combination with the higher MW chitosan generally showed marginally better dewatering performance.

Table 7.2 Sludge dewaterability with single and dual-conditioners

Type of conditioner	CST (s)	SRF $\times 10^{-13}$ (m/kg)	Cake solids content (%)
	Unconditioned sludge		
-	93.9	15.20	10.3
	Single conditioning aids (10 g/kg)		
Low MW chitosan only	35.0	1.71	26.6
Medium MW chitosan only	29.4	1.06	25.7
NaCl	68.6	3.72	12.8
KCl	59.2	3.48	12.6
$MgCl_2$	54.7	3.26	13.0
$CaCl_2$	39.5	3.49	13.3
$AlCl_3$	16.4	1.95	17.3
$FeCl_3$	12.0	1.86	16.5
	Single conditioning aid (5 g/kg chitosan)		
Low MW chitosan (control)	60.5	2.27	26.3
	Dual-conditioning aids (5 g/kg chitosan + 10 g/kg metal cation)		
NaCl	15.5	1.69	13.7
KCl	13.1	1.16	15.5
$MgCl_2$	12.0	0.70	17.7
$CaCl_2$	12.8	0.76	18.5
$AlCl_3$	9.3	0.57	20.6
$FeCl_3$	9.3	0.42	18.8
	Single conditioning aid (5 g/kg chitosan)		
Medium MW chitosan (control)	44.5	1.40	28.6
	Dual-conditioning aids (5 g/kg chitosan + 10 g/kg metal cation)		
NaCl	12.5	1.32	19.6
KCl	12.9	0.74	19.7
$MgCl_2$	11.3	0.46	14.9
$CaCl_2$	11.5	0.56	19.9
$AlCl_3$	9.5	0.24	19.7
$FeCl_3$	9.1	0.19	20.0

The combined doses of 5 g/kg chitosan and 10 g/kg metal cation in the dual-conditioning method gave higher level of dewaterability than the single dose of 10 g/kg chitosan. This indicates that the inorganic metal salts may substitute a portion of the polymer dosage while still attaining excellent dewaterability with reduced CST and SRF, but at the expense of dry cake solids content.

The comparison of cation effect on sludge dewatering performance is shown in Figure 7.2. Addition of Na^+ alone reduced the CST of raw sludge by 26.9% while dual-conditioning using chitosan and Na^+ reduced it by 83.5% and 86.7%, for the low and medium MW chitosans respectively. A similar trend was observed for K^+. For the divalent cations, although Ca^{2+} lowered the CST more than Mg^{2+} in single conditioning, that effect diminished when it was used in conjunction with chitosan. Al^{3+} and Fe^{3+} generally yielded better dewaterability than the other cations. When used with chitosan, the improvement was less noticeable than for the other cations as the "sole" use of these trivalent species had demonstrated remarkable dewatering performance. Considering the equivalent concentrations and the respective dewaterability values from Table 7.2, the effectiveness of metal cation(s) in sludge conditioning and dewatering may be presented in ascending order as: $Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Al^{3+} < Fe^{3+}$. Consequently dual-conditioning using chitosan and metal cations increased sludge dewaterability in a similar sequence.

A notable downside of dual-conditioning is that it cannot improve the cake solids content of dewatered sludge to the extent achieved by single conditioning using chitosan. As shown in Table 7.2, conditioning with the low MW chitosan increased the cake solids content from 10.3% (for dewatered sludge without conditioning) to 26.3% at a dose of 5 g/kg, but combination with metal cation yielded a lower cake solids content range of 13.7% to 20.6%, depending on the cationic species. Similar response was observed for the medium MW chitosan. This study has revealed that dual-conditioning may enhance the rate of dewatering as indicated by the CST and SRF results, but the resulting sludge cake may contain more trapped water compared to single conditioning using chitosan, thus reduced cake solids content was obtained.

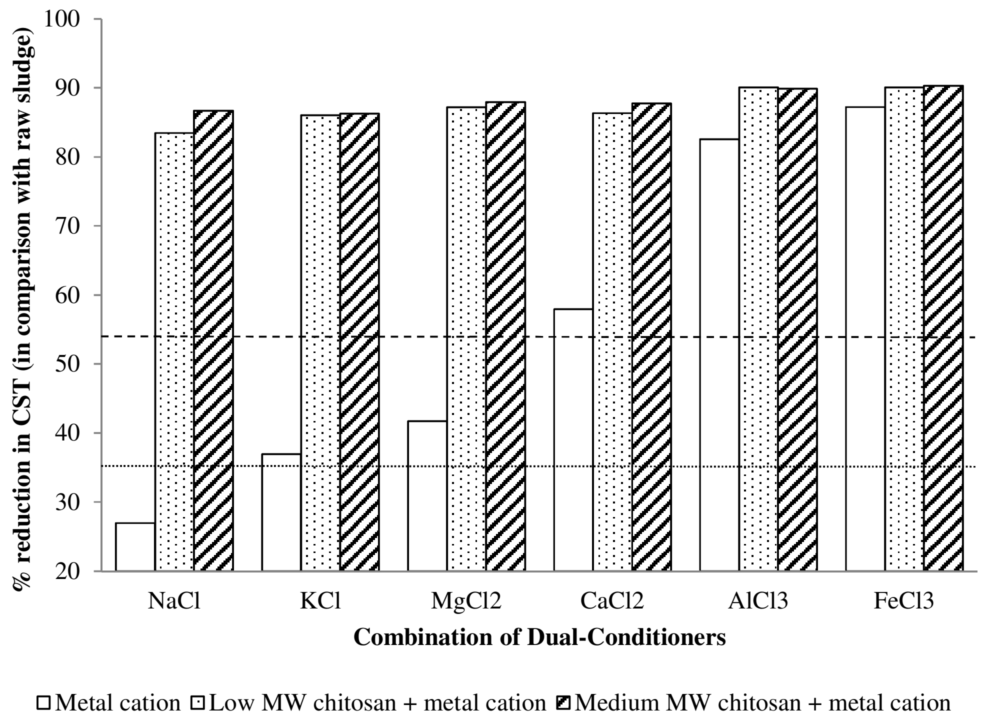


Figure 7.2 Effect of dual-conditioners on CST values, compared with raw sludge, in septic sludge system (dotted line: single conditioning with low MW chitosan; dashed line: single conditioning with medium MW chitosan)

(b) Dual-conditioning in anaerobic digested sludge

The dual-conditioning effect was examined in the AD sludge system at a fixed dose of 2.5 g/kg chitosan which was effective enough to reduce the CST by almost 50% in single conditioning. As shown in Figure 7.3, the trivalent Al^{3+} and Fe^{3+} were more effective than the monovalent and divalent cations in improving the sludge dewaterability in terms of CST reduction. When conditioned with Al^{3+} and Fe^{3+} alone, the CST values reduced by 43.9% and 41.3% respectively, compared with the unconditioned AD sludge. The increasing order of sludge dewaterability for each metal cation was noted as: $Na^{+} < Ca^{2+} < Mg^{2+} < Fe^{3+} < Al^{3+}$. Compared with the order of effectiveness for cationic species in the septic sludge (see Section 7.3.1), the sequence among divalent cations and trivalent cations was switched where Mg^{2+} and Al^{3+} performed better than their counterparts, Ca^{2+} and Fe^{3+} in sludge conditioning. Ozkan and Yekeler (2004) explained that Mg^{2+} was more effective on the coagulation of celestite suspension than Ca^{2+} at neutral pH because Mg^{2+} has a higher ionic potential (ionic charge/radius). This is in line with the findings of this study with AD sludge but is contrary to the ones of septic sludge. The findings of Sanin et al. (2006) support the latter where Ca^{2+} was found to produce a higher degree of improvement in sludge dewaterability when compared to Mg^{2+}. The performance of multivalent cations is likely to be dependent of the characteristics of the suspension medium. However, none of the metal cations used alone can reduce the CST as much as the single conditioning with chitosan as shown in Figure 7.3.

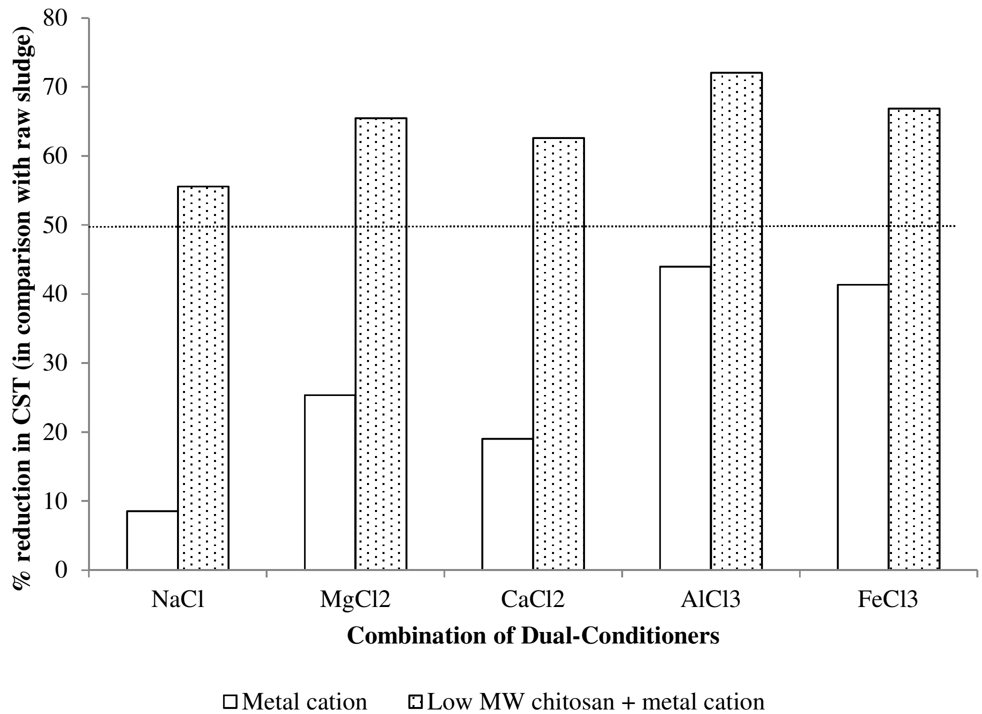
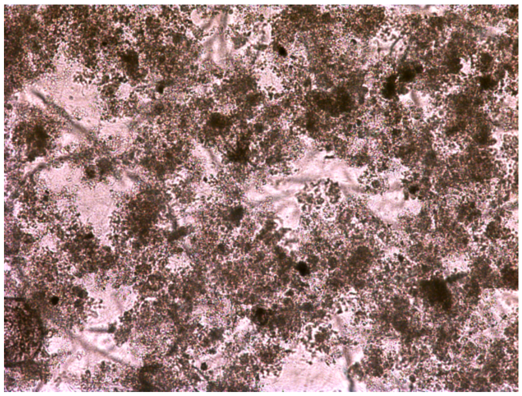
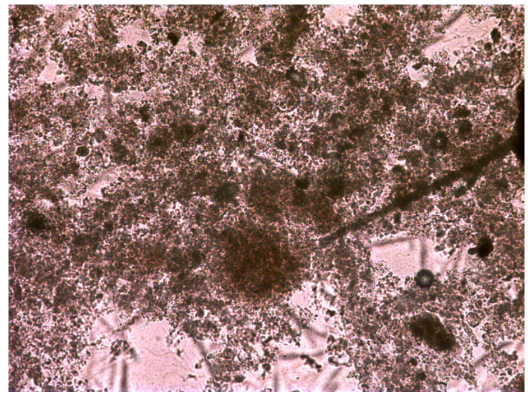


Figure 7.3 Effect of dual-conditioners on CST values, compared with raw sludge, in AD sludge system (dotted line: single conditioning with low MW chitosan)

Low MW chitosan was selected in this study as the conditioning polymer in order to feature the charge interactions proposed by Hogg (1999), where charge interactions are believed to be more important for low MW than for high MW polymers. It can be seen from Figure 7.3 that dual-conditioning of AD sludge using metal cations and chitosan improved sludge dewaterability variably depending on the cationic species. The combination of Al^{3+} and chitosan optimised the sludge dewaterability leading to a 72% CST reduction. Microscopic observation in Figure 7.4 pictured that the sludge dual-conditioned with Al^{3+} and chitosan formed larger and denser flocs with less trapped water compared with sludge conditioned using chitosan alone.



(a) AD sludge conditioned with chitosan



(b) AD sludge dual-conditioned with Al^{3+} and chitosan

Figure 7.4 Images of AD sludge flocs formed under the single conditioning and dual-conditioning effects

(c) Mechanisms of dual-conditioning

Both the septic sludge and AD sludge applied in this study are considered to be treated and decomposed in the absence of oxygen. The septic sludge is usually characterised by a black colour and rotten-egg odour. It is produced in a simple septic tank under unheated and unmixed condition which is applicable for small facilities (Spellman 2009). The AD method however involves complex equipment and carefully controlled operation in a common two-stage digestion process. The destruction of the organic matter during AD breaks down the solid material and produces finer particles. Therefore AD sludge contains mainly the non-biodegradable fraction of the sludge and is more homogeneous in structure (Houghton et al. 2000). The colloidal nature of the digested biological sludge along with the increase in soluble proteins and polysaccharides as a result of AD often impede the sludge dewaterability and increase the polymer conditioning requirements (Novak 2010).

The conditioning results obtained in this study will thus form the basis for further investigation into the application of dual-conditioning aids to enhance the dewatering performance while reducing the polymer demand for AD sludge.

The idea of combining metal cations and chitosan polymer as dual-conditioners is based on the concept that the destabilisation can be accomplished by addition of cations which allows small flocs to form; at the same time, the bridging action from polymer serves to link these flocs into substantially larger units. To understand the concept better, it is vital to examine the mechanisms governing the different dewatering performances of cations. The improvement in sludge dewatering properties due to cation addition could be explained by many things. In most cases, the addition of cations is expected to improve sludge dewaterability. The classical Double Layer or Derjaguin-Landau-Verwey-Overbeek (DLVO) theory describes charged particles as having a double layer of counter-ions surrounding them (Sobeck and Higgins 2002). This double layer or cloud repels adjacent particles and inhibits aggregation. It is therefore anticipated that the addition of cations will increase the solution's ionic strength and compress the double layer, thereby improving bio-flocculation, settling and dewatering properties. Several researchers have performed experiments that support the DLVO theory for the role of cations in bio-flocculation (Liu et al. 2012, Sobeck and Higgins 2002, Lo et al. 2001, Cousin and Ganczarczyk 1998, Zita and Hermansson 1994).

On the other hand, there are different opinions on the effect of cation valency on the binding properties of negatively charged sludge particle surface, which in turn affects sludge dewaterability. According to Sanin et al. (2006), potassium (and other monovalent ions) does not improve the floc structure as much as the divalent cations such as Ca^{2+} and Mg^{2+}. This may be explained by their inability to form linkages between the extracellular polymeric substances (EPS) within the sludge matrix and floc surfaces due to their monovalent nature. The researchers also believe that the increase of osmotic pressure due to increasing K^+ in the medium may cause more ions transferred into the cell to maintain the cell's osmotic pressure. Thus monovalent cations gave a negative impact on the dewaterability of activated sludge in their study.

Although monovalent cations lack a binding role within the sludge floc, Lo et al. (2001) believe that their presence in the sludge might cause a salting out effect, which in turn helps release bound water from the flocs to the bulk solution. Erdincler and Vesilind (2000) also suggest that the biological sludge cells could be disrupted by Na^+, so that water flows out and the cell tends to shrink due to the osmotic effect. The findings of the present study seem to be in agreement with the positive impact of monovalent cations although the response is not as pronounced as divalent and trivalent cations. Better dewaterability (decreases in CST and SRF) was observed with the addition of monovalent cations in this work. However, the solids content of the filtered sludge cake did not show significant improvement, probably due to extra water-binding surfaces created by cell disruption, leading to a net increase in the vicinal water content of sludge samples.

For divalent cations, greater improvement in sludge dewaterability due to Ca^{2+} and Mg^{2+} addition could be due to the bridging of negatively charged functional groups in the sludge creating a more tightly bound floc matrix, as suggested by the Divalent Cation Bridging (DCB) theory (Sobeck and Higgins 2002). This suggests that divalent, rather than monovalent, cations can bridge negatively charged functional groups within the EPS present in sludge. Sludge dewaterability is closely related to sludge floc-forming ability. The results of this study show that Ca^{2+} and Mg^{2+} improve dewaterability (or filterability), which is believed to happen due to the improved floc formation according to the DCB theory. In addition, the alginate theory proposed by Bruus et al. (1992) suggests that alginate may be present in sludge, and, since alginate aggregation is specific for Ca^{2+}, the researchers infer that the better dewaterability demonstrated by Ca^{2+} arises from the greater affinity of the sludge suspension for Ca^{2+} than Mg^{2+} (Sobeck and Higgins 2002). This explains why Ca^{2+} is more effective than Mg^{2+} in enhancing sludge dewaterability in septic sludge but not in AD sludge for this study as the presence of alginate may diminish after the digestion process (see Figures 7.2 and 7.3). In fact, Ca^{2+}, in the form of lime, is commonly used as a conditioner in dewatering units to improve dewaterability, indicating that the positive effect of Ca^{2+} has been known for a long time (Sanin et al. 2006).

Trivalent aluminium and ferric salts may act by a sequence of hydrolysis, adsorption, and precipitation reactions in sludge conditioning (Dentel 2001). Upon dissociation,

Al^{3+} and Fe^{3+} may form cationic hydrolysis products that are strongly adsorbed on negatively charged particles and can give effective destabilisation due to the extensive network bridging as a result of more cationic sites from these trivalent cations. Dentel (2001) points out that conditioning using aluminium or ferric salts alone is inadequate due to the properties of the associated hydroxides, which are hydrophilic, amorphous, and compressible, leading to a slurry that retains water and yields under shear. This can be observed from Table 7.2 that single conditioning using Al^{3+} and Fe^{3+} gave lower cake solids content (thus higher moisture content) than polymer conditioning even though their CST values were the lowest.

The findings from the dual-conditioning study reveal that chitosan polymer and trivalent cations had very positive effect on the treated sludge in both the single and dual-conditioning methods. Less intense improvement was observed for Al^{3+} and Fe^{3+} when used together with chitosan, as the single conditioning using these trivalent species had demonstrated significantly enhanced dewaterability as given in Table 7.2. The enhanced dual-conditioning effect was more noticeable for monovalent and divalent cations compared to trivalent cations. The effectiveness of dual-conditioning was significantly affected by the cationic nature of the inorganic metal salts and therefore the dewatering behaviour can be explained using the similar double layer compression, salting out effect, cell disruption, as well as ion bridging mechanisms, coupled with polymer bridging.

7.4 Conclusion

This study affirms an encouraging improvement in sludge dewaterability when the organic chitosan and inorganic metal cations are used in the dual-conditioning of sludge. The range of 15–20 g/kg chitosan was the optimum chemical dosage for both the low MW and medium MW chitosans applied in the single conditioning of septic sludge. When used in conjunction with 10 g/kg of trivalent aluminium and ferric cations, both the chitosans reduced the CST and SRF to the lowest values at a reduced dose of 5 g/kg. The results however indicate a higher rate of water removal at the expense of dry solids content in dual-conditioning as compared with the single use of chitosan polymer. It is thought that neutralisation of the sludge surface charge with double layer compression, salting out effect with cell disruption and bridging of the colloidal particles arising from the addition of cations, all contribute to the enhanced dewatering performance, along with polymer bridging induced by chitosan. The probable formation of trivalent hydroxides in polymer conditioned sludge may, however, reduces the solids content of the filtered sludge cake owing to their hydrophilic, amorphous and compressible nature. With careful economic evaluation, it is still possible to improve sludge dewaterability by dual-conditioning using the nontoxic biopolymer chitosan, with the cheaper inorganic chemicals, to reduce the polymer demand, as well as to address concerns about polymer toxicity.

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CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

Chemical conditioning aims to improve sludge dewatering and cake forming properties in dewatering processes. Treated sludge should have the desired characteristics of high dewaterability and high cake concentrations or percentage solids capture with chemical addition. The findings in this study have demonstrated the effectiveness of different organic and inorganic chemical conditioning aids and measurement parameters used to predict the performance and to optimise the chemical dosage in dewatering of anaerobically digested (AD) sludge and synthetic sludge. Results also reveal the innovative prospect of dual-conditioning of sludge using the eco-friendly biopolymer, chitosan, combined with some cheaper metal cations as a feasible dewatering choice.

8.1 Characterisation Studies of AD Sludge and Synthetic Sludge (Chapter 4)

From the characterisation studies, most of the physical and chemical properties of the AD sludge applied in this work were comparable with those of literature except for the higher values of mean particle size and zeta potential (ZP) which fell within the range of 80–100 μm and –12 to –14 mV respectively. The AD sludge thus consisted of bigger floc particles with reduced surface-to-volume ratio and hence reduced negative surface charges. Due to the concerns of variation in sludge characteristics and prevention of possible biological hazard in analytical laboratory, a chemically well-defined synthetic sludge was proposed for further studies. Modification was made to the published synthetic sludge formulation using medium fibrous cellulose to replace microcrystalline cellulose because of its size and shape resemblance to the filamentous bacteria. The modified synthetic sludge was able to simulate most of the physicochemical properties of the AD sludge such as the solids content, dewaterability (or filterability), particle size, pH and ZP value, which are important in the study of dewatering performance. In particular, the capillary suction time (CST) as the primary dewaterability parameter was attained at 120–160 s for the synthetic sludge which was close to the one of AD sludge. The sludge morphology study illustrated the collection of yeast particles as bacterial colonies captured within a structure held together with filamentous organisms in the synthetic sludge. Besides, the synthetic sludge exhibited a non-Newtonian behaviour which followed the power-law model, $\tau = K\dot{\gamma}^m$ with the best fit results at the average K value of 0.0289 and m of 0.5775. This was consistent with the shear-thinning behaviour of most AD sludge. Therefore, it can be concluded that the modified synthetic sludge in this work mimicked the AD sludge to a considerable extent for the purpose of dewatering study.

8.2 Dewaterability Studies (Chapter 5)

8.2.1 Effects of molecular weight and dosage of polymer on sludge dewatering

In this study, enhanced sludge dewaterability was indicated by a decrease in CST. With increasing conditioner dosage, the CST decreased rapidly and eventually reached a plateau for both the low molecular weight (MW) and medium MW chitosans applied in AD sludge conditioning. The MW of a polymer has two opposing effects on the sludge dewatering performance. Increase in MW of a polymer introduces more cationic sites for binding of sludge particles and network bridging, but its long polymeric chains may tend to adsorb only on the outside of the sludge flocs resulting in more trapped waters and hence wetter sludge cake properties. On the other hand, the shorter polymer molecules may diffuse more readily and adsorb onto the sludge particles but the floc size and floc strength may suffer to some extent. For the synthetic sludge, the sludge dewaterability followed a similar trend of decreasing CST till a plateau with increasing conditioner dosage.

The CST parameter was correlated to the measurements of supernatant turbidity, electrical conductivity, ZP, filtered cake solids content and floc size using synthetic sludge as controlled experiments to determine the optimum chemical dosage in sludge conditioning. The results suggest that the range of 15–20 g/kg chitosan was the optimum dosage for this study where the CST, turbidity and cake solids content were attained between 6.6–11.0 s, 35.4–40.6 NTU and 24.3–25.3% respectively. Charge reversal was found at the dosage of 20 g/kg chitosan where the ZP value reached 21 mV but no deterioration was observed for the CST and turbidity values at this point. ZP may not give a reliable prediction of optimum dosage for good conditioning when both charge neutralisation and polymer bridging mechanisms are governing but it does provide important information about the conditioning mechanism. Further increase in conditioner dosage led to overdosing and the dewaterability decreased.

8.2.2 Effect of organic and inorganic compounds in sludge conditioning

Both organic polymers and inorganic trivalent metal salts demonstrated remarkably high dewaterability in the present sludge conditioning study. When applied in the AD sludge, the CST values reduced by 41–62% for aluminium chloride, ferric chloride, EMA 8845 and PAC. Synthetic sludge conditioned with aluminium chloride, ferric chloride, PAC, medium MW and low MW chitosans demonstrated superior dewaterability where the CST values reduced by 91–95%. The cationic nature of these organic and inorganic chemicals reversed the cell surface charges most effectively and enhanced dewaterability. The polymeric feature of organic polymers further flocculated the sludge via polymer bridging which aided the formation of larger flocs. The monovalent cations improved the dewaterability to a lesser extent as they lacked binding role in sludge flocculation. The divalent cations performed better than the monovalent cations with more cationic sites for bridging. Trivalent cations prevailed over the other cations because of their increased cationic ability in adsorption and extended bridging.

8.2.3 Effects of pH, temperature and mixing conditions on sludge dewatering

The sludge dewaterability increased with decreasing pH. Without addition of chitosan conditioner, sludge treated with hydrochloric acid alone showed enhanced dewaterability significantly by reducing the CST to 12.8 s at pH 2.3 with high solids content of 25.4%. The model derived from the response surface method (RSM) design indicates that the change in pH gave more impact to sludge dewaterability compared to the dosage effect. Acidic pH enhances sludge dewatering because it promotes the ionisation of the amine groups of organic polymers and suppresses the negative surface charges carried by the sludge particles, in addition to possible cell disruption and desorption of the extracellular polymeric substances (EPS) which release more bound water. Temperature effect was less pronounced on sludge conditioning process in this study. As for the mixing effect during the flocculation step, both intense and extended mixing placed a dampening effect on the sludge dewatering and formation of flocs. Restabilisation and rupture of floc structure could be the reasons of deterioration in sludge dewaterability in this case.

8.2.4 Mechanisms of conditioning

Both charge neutralisation and bridging are the two very important conditioning mechanisms to explain the role of organic polymers and inorganic metal cations in enhancing sludge dewatering. In most cases, charge neutralisation is a prerequisite to effectively destabilise the sludge suspension as seen from the ZP results in this study. Polymer bridging further enhances dewatering by the adsorption of polymeric molecules on sludge particles with their long and extended cationic sites binding to more particles. In addition, this study revealed that charge reversal or restabilisation did not significantly affect the sludge dewaterability at the optimum polymer dose. This led to the hypothesis that the favourable adsorption of polymer molecules onto the sludge particles and bridging overwhelmed the succeeding effect of charge repulsion.

For inorganic metal cations, it is believed that the addition of cations, especially monovalent cations like Na^+ and K^+, may increase the solution ionic strength and compresses the double layer of counter-ions which initially prevents coagulation. The salting out effect and cell disruption due to the addition of Na^+ and K^+ may also release the bound water and improve the dewatering properties. These mechanisms are less significant when compared to the bridging effect of divalent charges according to the Divalent Cation Bridging (DCB) theory. Trivalent metal cations are the most effective inorganic conditioners as they may form cationic hydrolysis products that are strongly adsorbed on negatively charged particles and give effective destabilisation through the extensive network bridging.

8.3 Rheological Studies (Chapter 6)

Initial studies on sludge sampling location in a rheological rotational test revealed that the sludge should be sampled from a well-mixed suspension in order to explore the sludge rheological behaviour in the presence of fluid-floc interaction. The acquired rheogram data indicate that the raw or unconditioned synthetic sludge exhibited shear thinning behaviour that followed the power-law model, $\tau = K\dot{\gamma}^{m}$. Conditioned sludge sampled from the fluid phase exhibited an excellent fit of the Bingham model, $\tau = \tau_0 + \eta\dot{\gamma}$ but the suspended sludge and settled sludge after conditioning were difficult to model as a result of destructible polymer-sludge network strength under shear.

Increase in conditioner dosage enhanced sludge resistance to flow and network strength as indicated by the increase in viscosity, yield stress and peak height in the rheogram obtained from the rheological rotational test. The dosage of 20 g/kg chitosan was selected as the optimal dosage rather than 15 g/kg due to the improved rheological behaviour in reasonable agreement with the optimum dewaterability results. Hence rheology can be used as a tool to optimise the chemical dosage in sludge conditioning and dewatering when used in conjunction with sludge dewaterability parameters. Both high-shear viscosity and yield stress have been applied as a useful indicator for the sludge's network strength to optimise the chemical dosage in this study. Rheogram peak value may be used as a tool to optimise the chemical dosage with caution in taking the peak readings.

From the rheological studies, it was also found that inorganic chemicals exhibited favourable network strength of one to two orders higher than the ones of organic chemicals although both chemicals demonstrated good dewaterability when used in sludge conditioning. Besides, acid treatment significantly enhanced the sludge shear resistance to flow while enhancing the dewatering performance. Meanwhile change in temperature gave more impact to sludge rheology compared to sludge dewaterability but the effect of mixing conditions was minor in both sludge rheology and dewaterability.

8.4 Application of Single and Dual Conditioning Aids (Chapter 7)

Compound use of organic polymer and inorganic metal salt in dual-conditioning of sludge has significantly improved the sludge dewaterability at the expense of the resulting cake solids content. The optimal results were obtain at the combined doses of 10 g/kg trivalent metal salt (i.e. chloride salt of Al^{3+} and Fe^{3+}) and 5 g/kg chitosan where the CST, SRF and cake solids content were attained between 9.1–9.5 s, 0.19–0.57×10^{13} m/kg and 18.8–20.63% respectively. The enhanced dual-conditioning effect was more evident for the monovalent and divalent cations compared with the trivalent cations. The effect of MW became less when chitosan was used in conjunction with cations where the medium MW chitosan showed marginally better dewatering performance than the low MW chitosan in dual-conditioning. The dual-conditioning method is believed to function via enhanced charge neutralisation with double layer compression, more water release from salting out effect along with cell disruption, and bridging of the colloidal particles, accompanied by polymer bridging, which add up to a profound impact to enhance the sludge dewaterability.

8.5 Recommendations for Future Work

The present study has proven the effectiveness of a number of organic and inorganic conditioning aids in enhancing the sludge dewatering performance and rheological behaviour. However there are a few issues that need to be addressed in order to supplement the current study and hence the following recommendations are proposed for extended study.

8.5.1 Dewaterability studies

- Although chitosan as a pseudo-natural cationic polymer has shown high potential to enhance sludge dewaterability in this work, in practice, sludge conditioning evaluations should be conducted on the actual sludge in the full-scale operations. Therefore a number of the dewaterability and rheological parameters applied in this study should be fully tested on the actual sludge and on site whenever possible. Besides, the impact of high-shear and high-pressure dewatering operations may present another challenge to the existing data which were obtained from vacuum filtration dewatering. Further comparative evaluations may be performed on high-shear dewatering devices such as centrifuge and high-pressure dewatering devices such as filter press.

- The structures and characteristics of chitosan may be manipulated to enhance its coagulation and flocculation properties in sludge conditioning. Chitosan polymer in a branched configuration may provide a stronger floc structure but the polymer dose requirements may increase. On the other hand, increased charge density in the cationic chitosan polymers may facilitate the coagulation of the negatively charged sludge particles but these highly charged polymers develop a more linear structure with limited structural flexibility due to repulsion between sites (Dentel 2010). Besides, chitosan produced from waste shells of shrimps and crabs with lower purity may be tested for its application in sludge conditioning to reduce the chemical cost.
- Further investigation should be performed on the safety and environmental effect of the entrapped conditioning chemicals in the cake solids from dewatering. Both the beneficial use as biosolids and non-beneficial disposal of sludge after the treatment process should meet the regulated requirements in order to protect human health and the environment.

8.5.2 Rheological studies

This work has attempted to obtain the rheological measurements on the sludge suspensions based on the flow or shear measurements which are the simplest to carry on and have been widely studied. Dynamic measurements with sinusoidal oscillations may be performed to complete the information obtained from flow measurements (Seyssiecq et al. 2003). The flow measurements characterise the structure of the suspension for its viscous and plastic properties whereas dynamic measurements characterise viscoelastic properties of the material and determine the limit between viscoelastic and plastic behaviours. Besides, the thixotropic nature of sludge, which is its time-dependant behaviour, should be considered as well for process optimisation. The thixotropic behaviour would result in structural build-up of sludge over a long retention time and form dead zone in the mixing tank if not sheared properly. Change of flow behaviour of sludge over time is also an important factor in pipeline and pumping system design as it can alter the pipe flow with clog formation when the wall shear stress is below a critical shear to maintain a homogenous flow (Eshtiaghi et al. 2013).

8.5.3 Application of dual-conditioning aids

There are more aspects to be explored in terms of the relationship between dewaterability, rheological and physicochemical properties, as well as floc size and strength for the application of dual-conditioning aids in sludge dewatering. Although the effect of the polymer's MW in dual-conditioning seems nominal when applied to filtration dewatering for this study, it should be noted that a lower MW polymer provides efficient flocculation but much lower floc resilience than a higher MW polymer, which is important for high-shear separation processes. In addition, floc strength may alter to some extent due to the partial substitution of polymer by inorganic metal salt in dual-conditioning. Further studies should therefore look into the dual-conditioning effect in high-shear dewatering operations such as centrifugation. The economic benefit gained using the cheaper metal salt to supplement polymer should also be assessed against the resulting inferior cake properties in order to optimise the dual-conditioning method.

References

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Eshtiaghi N., Markis F., Yap S.D., Baudez J.C., and Slatter P. 2013. "Rheological characterisation of municipal sludge: a review." *Water Research* 47 (15):5493-510.

Seyssiecq I., Ferrasse J.-H., and Roche N. 2003. "State-of-the-art: rheological characterisation of wastewater treatment sludge." *Biochemical Engineering Journal* 16 (1):41-56.

APPENDIX A

SAMPLE CALCULATION AND CALIBRATION

A.1 Calculation of Specific Resistance to Filtration and Cake Solids Content

This section presents a sample calculation for the Specific Resistance to Filtration (SRF) value and cake solids content for a raw synthetic sludge sample of the average total solids of 15.5 g/L. As described in Section 3.4.2, the sludge sample was poured onto the Buchner funnel in the modified filtration system with applied vacuum pressure of 50 kPa. The volume of filtrate collected within the graduated cylinder was timed with a stopwatch and the results were tabulated in Table A.1.

The filtered sludge cake retained on the filter paper was used to determine the cake solids content following filtration dewatering. This was done by overnight heating in oven at 103–105°C. The following data was obtained.

Weight of filter paper, W_0 = 2.0253 g

Weight of wet filtered cake and paper, W_1 = 3.0478 g

Weight of dried cake and paper, W_2= 2.1205 g

Volume of total filtrate collected, V^t = 6.4 cm^3

The data was then used to determine SRF (m/kg) using Equation A.1.

$$\mathrm{SRF} = \frac{2A^2 \Delta P b}{\eta w} \tag{A.1}$$

Table A.1 Volume of filtrate collected with filtration time for SRF calculation

Filtration time, *t* (s)	**Volume of filtrate, *V* (cm^3)**	***t/V* (s/cm^3)**
15	1.8	8.3
23	2.0	11.5
30	2.3	13.0
45	2.7	16.7
60	3.0	20.0
75	3.2	23.4
90	3.3	27.3
105	3.4	30.9
120	3.6	33.3
135	3.6	37.5
150	3.7	40.5
165	3.8	43.4
180	3.9	46.2
210	4.1	51.2
240	4.2	57.1
270	4.3	62.8
300	4.5	66.7
360	4.7	76.6
420	4.9	85.7
480	5.1	94.1
540	5.2	103.8
600	5.4	111.1

Knowing that the diameter of funnel (and filter paper) is 47 mm, and assuming that the viscosity of filtrate is close to the one of water which is 0.89 mPa.s at 25°C, therefore

Filtration area, $A = \pi r^2 = 3.142 \times (0.047/2)^2 = 1.735 \times 10^{-3}$ m^2

Applied vacuum pressure, ΔP = 50 kPa = 5.0×10^4 N/m^2

Dynamic viscosity, η = 0.89 mPa.s = 0.89×10^{-3} N.s/m^2

Weight of dry cake per unit volume of total filtrate collected at the end of filtration, $w = (W_2 - W_0) / V^t =$ 14.9 kg/m^3

The coefficient b (s/m^6) was obtained from the initial linear slope of the plot of the filtration time-to-filtrate volume ratio (t/V) versus V itself as shown in Figure A.1.

Coefficient b = 9.9664 s/cm^6 = 9.9664×10^{12} s/m^6

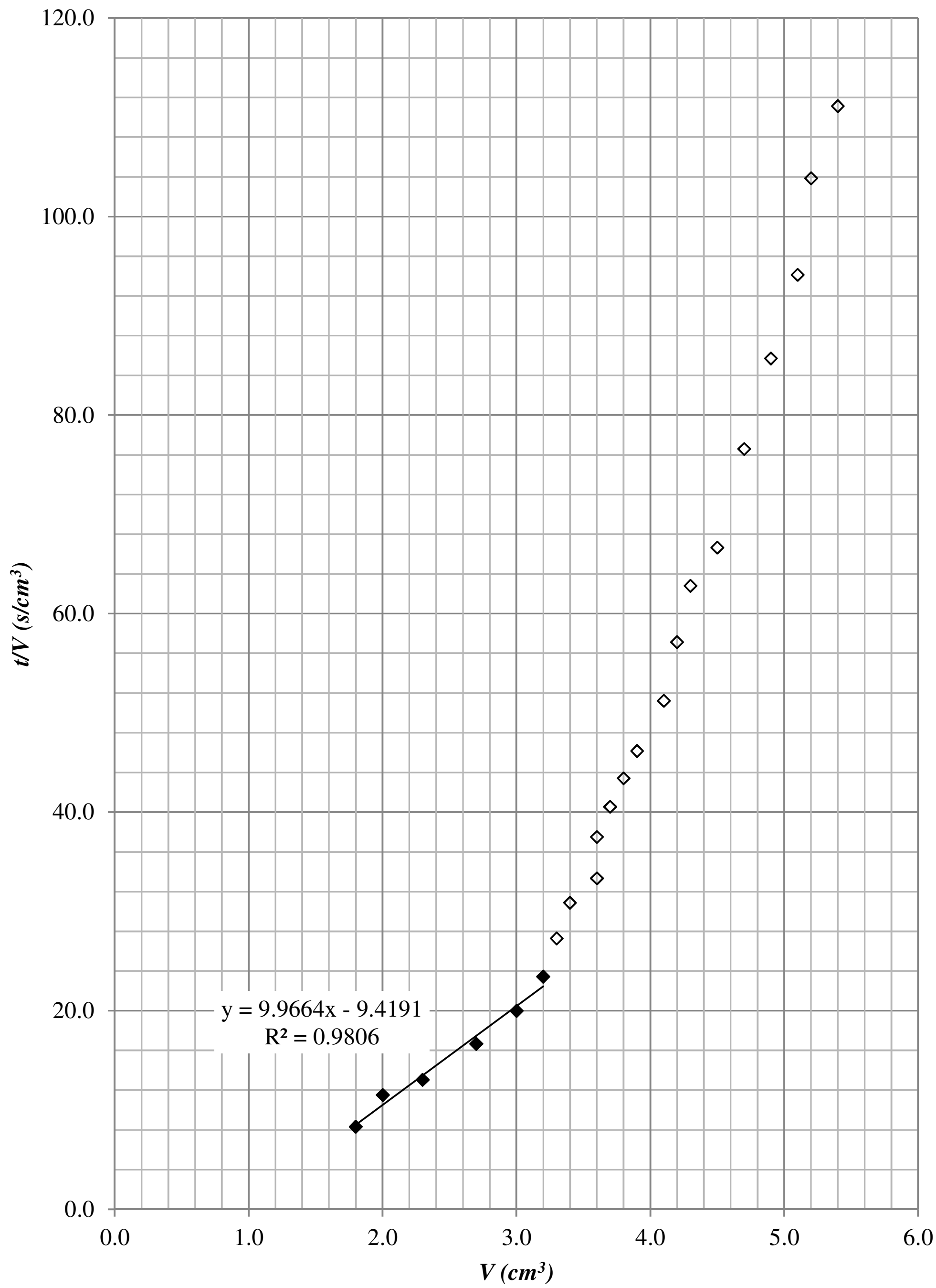

Figure A.1 Filtration time-to-filtrate volume ratio (*t/V*) versus *V* for the determination of coefficient *b* in SRF calculation

Hence,

$$\begin{aligned}
\text{SRF} &= \frac{2A^2 \Delta P b}{\eta w} \\
&= \frac{2\left(1.735\times10^{-3}\right)^2\left(5.0\times10^{4}\right)\left(9.9664\times10^{12}\right)}{\left(0.89\times10^{-3}\right)\left(14.9\right)} \\
&= 2.27\times10^{14}\ \text{m/kg}
\end{aligned}$$

The percentage of cake solids content was calculated using Equation A.2.

$$\text{Cake solids content} = \frac{W_2 - W_0}{W_1 - W_0}\times 100 \qquad \text{(A.2)}$$

$$\text{Cake solids content} = \frac{2.1205 - 2.0253}{3.0478 - 2.0215}\times 100 = 9.3\%$$

A.2 Calibration of Turbidity

To predict the out-of-range reading for very turbid supernatant, a sample of raw synthetic sludge with known total solids (TS) content of 15.61 g/L was diluted few times for calibration of turbidity. As presented in Table A.2, the turbidity reading was recorded for each time of dilution. The number of dilution, *n*, indicates that the sludge sample was diluted by half each time. The data was plotted in Figure A.2 to obtain the correlation between the turbidity and the TS content of diluted sludge sample. From the calibration curve in Figure A.2, a linear equation $y = 417.1x - 20.1$ was obtained.

Table A.2 Dilution of sludge sample for turbidity reading

TS (g/L)	Number of dilution, n	Turbidity (NTU)
15.61	0	Out of range
7.81	1	Out of range
3.90	2	Out of range
1.95	3	812.0
0.98	4	359.0
0.49	5	166.5
0.24	6	75.9
0.12	7	32.4
0.06	8	18.7
0.03	9	10.3

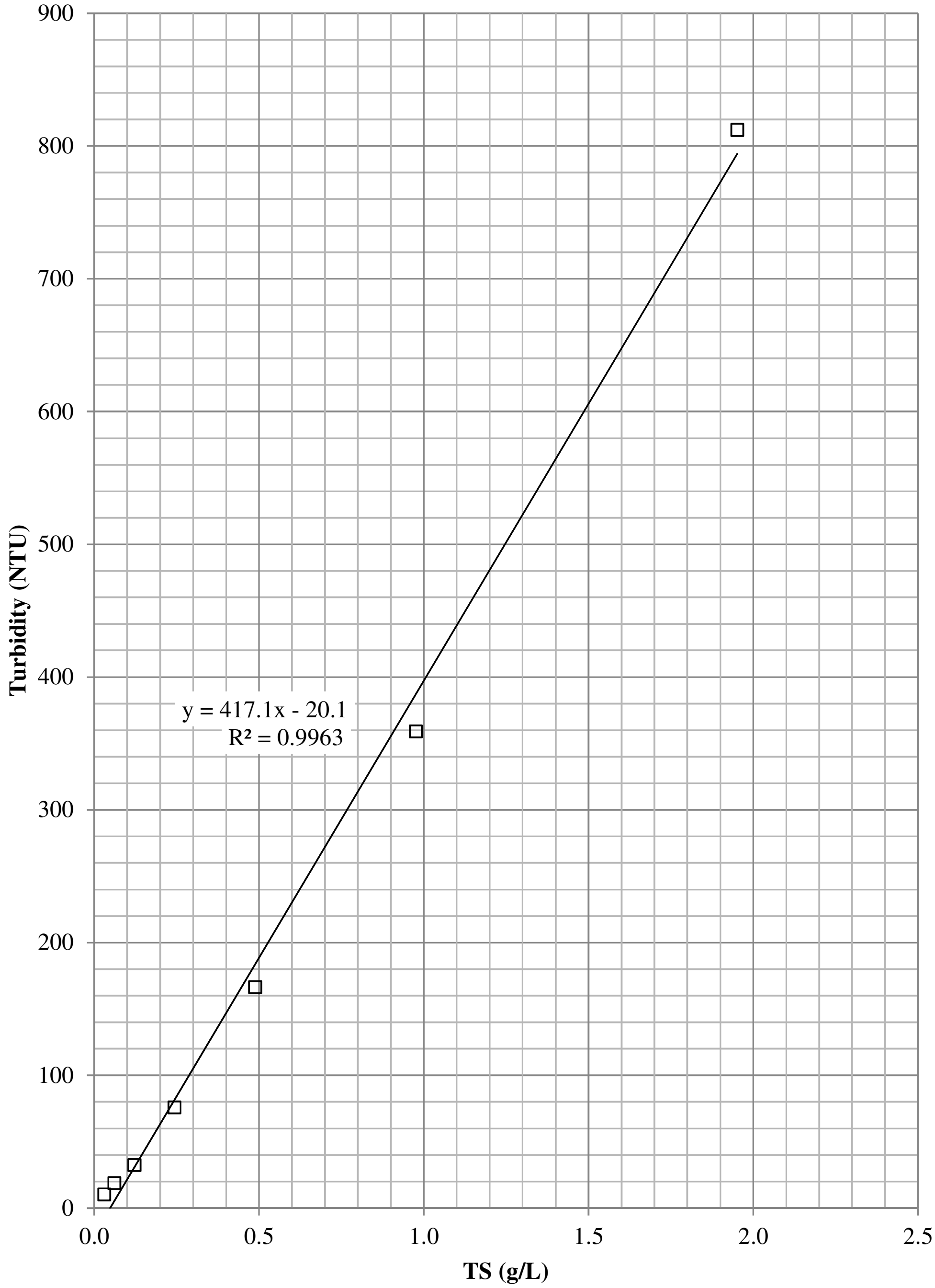

Figure A.2 Turbidity value versus total solids (TS) of diluted sludge sample for calibration

Taking

T_0 = turbidity after dilution

T = calibrated turbidity

x_0 = TS of sludge sample after dilution

x = TS of sludge sample

n = number of dilution

Therefore

$$x_0 = \frac{x}{2^n} \tag{A.3}$$

$$T_0 = 417.1x_0 - 20.1 \tag{A.4}$$

$$T = 417.1x - 20.1 \tag{A.5}$$

Substitute Equations A.3 and A.4 into Equation A.5,

$$T = 417.1(2^n)\left(\frac{T_0 + 20.1}{417.1}\right) - 20.1$$

$$T = 2^n(T_0 + 20.1) - 20.1 \tag{A.6}$$

Equation A.6 was used to predict out-of-range turbidity reading in Section 3.4.3.

APPENDIX B

RHEOLOGICAL DATA

B.1 Rheograms of Conditioned Sludge

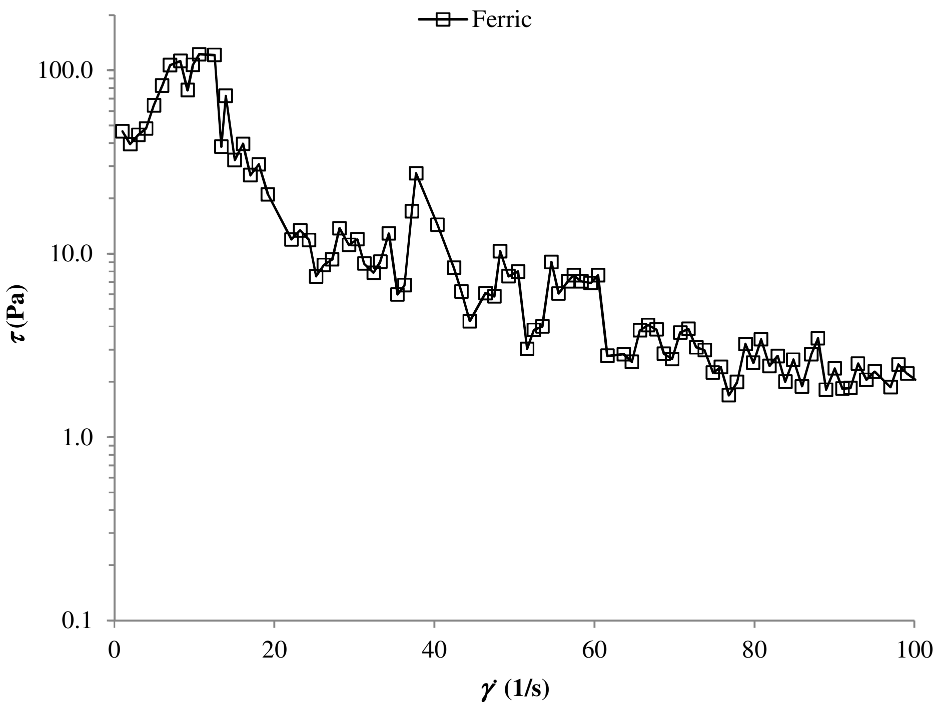

Figure B.1 Rheogram of conditioned sludge at 15 g/kg of ferric chloride

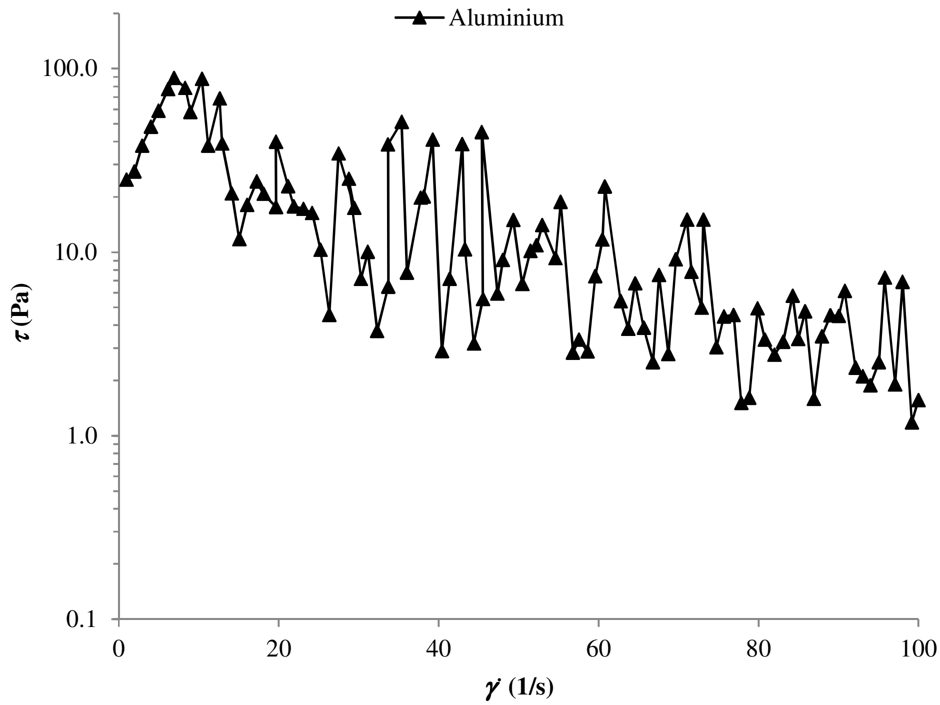

Figure B.2 Rheogram of conditioned sludge at 15 g/kg of aluminium chloride

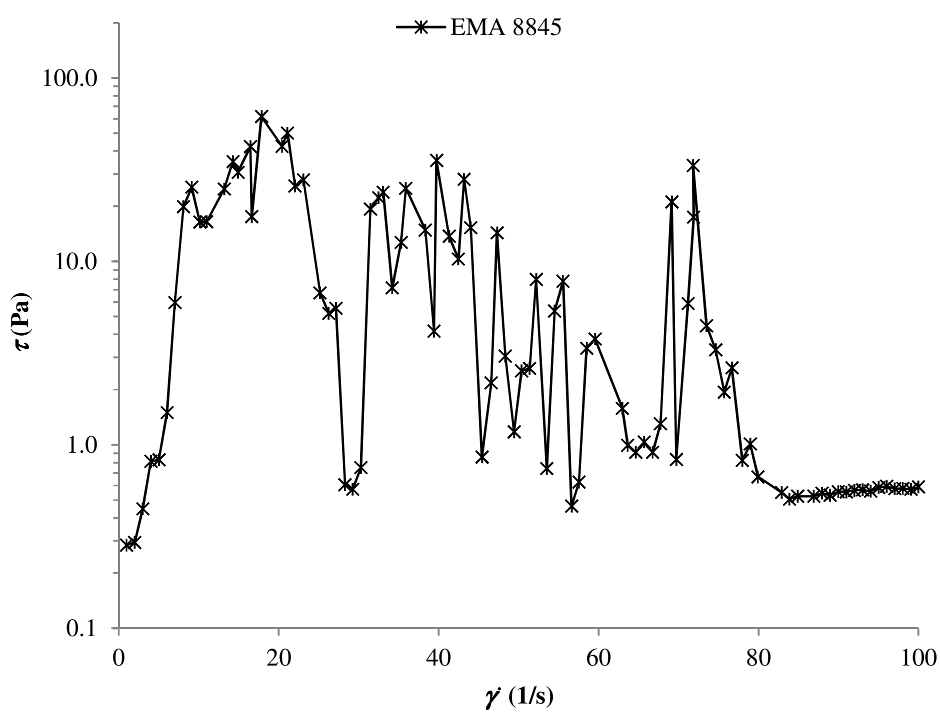

Figure B.3 Rheogram of conditioned sludge at 15 g/kg of EMA 8845

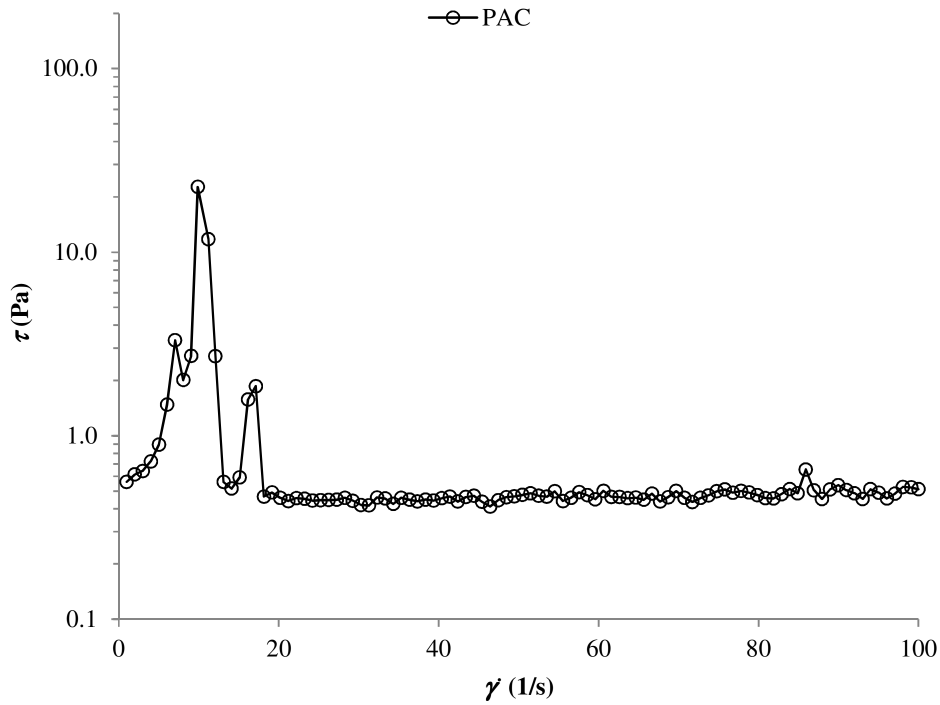

Figure B.4 Rheogram of conditioned sludge at 15 g/kg of PAC

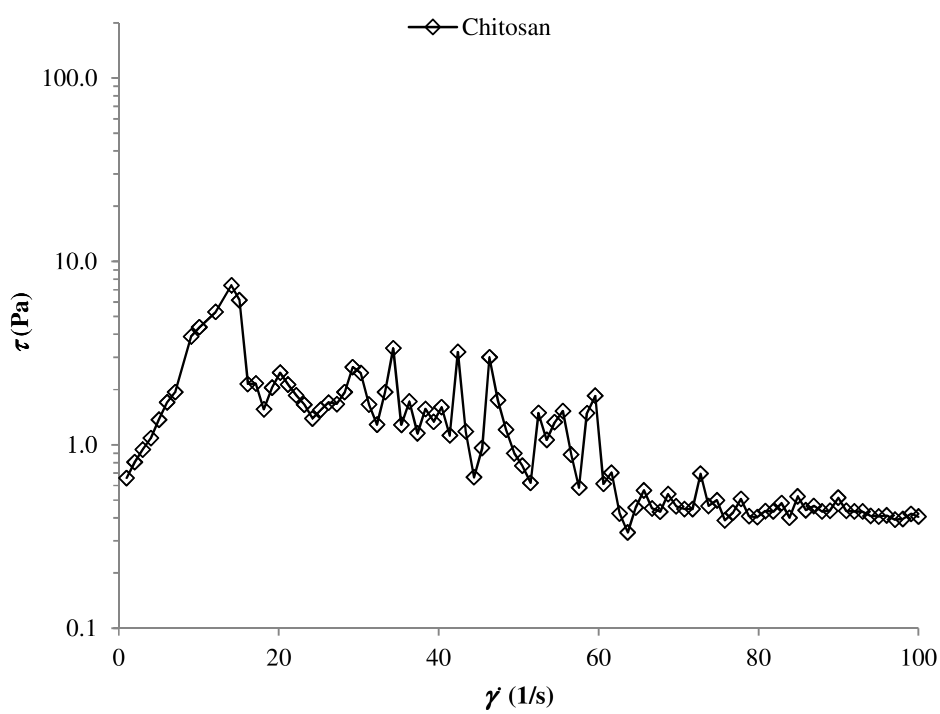

Figure B.5 Rheogram of conditioned sludge at 15 g/kg of chitosan

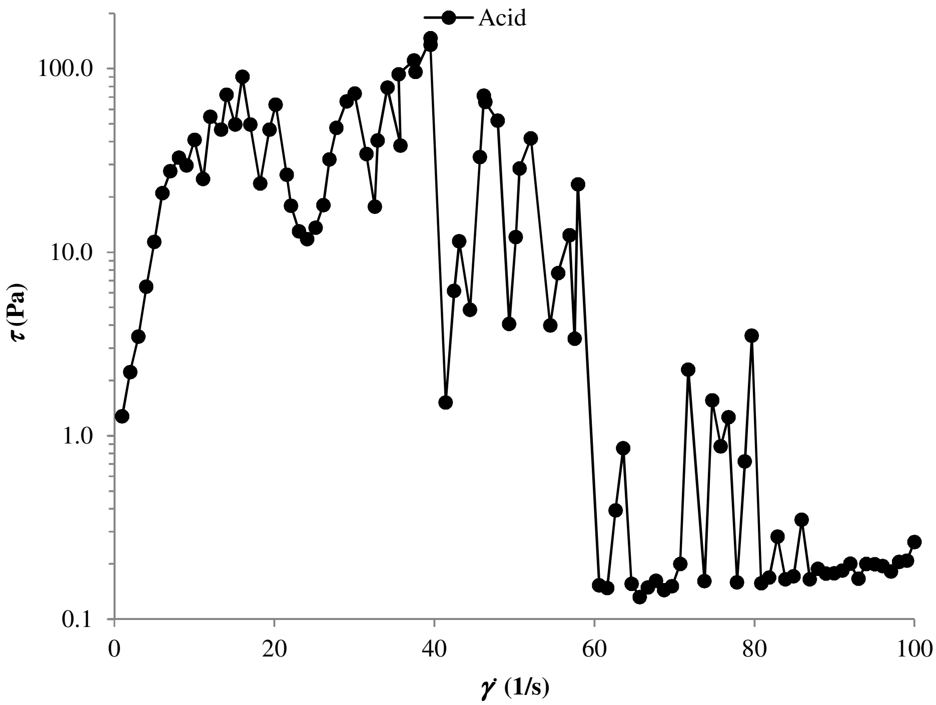

Figure B.6 Rheogram of conditioned sludge at 15 g/kg of hydrochloric acid

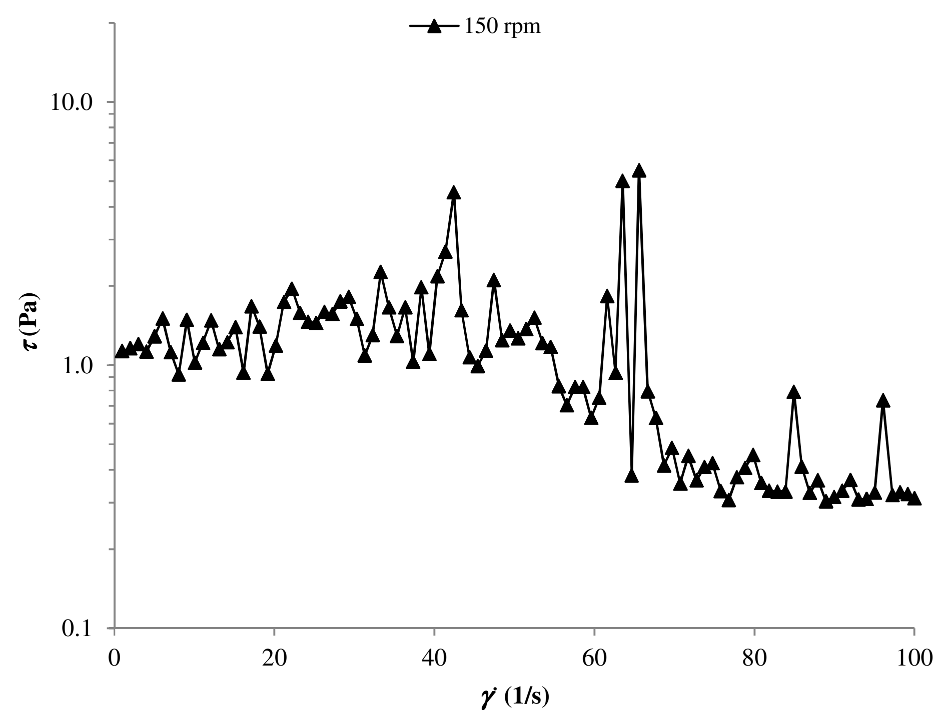

Figure B.7 Rheograms of conditioned sludge at the mixing speed of 150 rpm

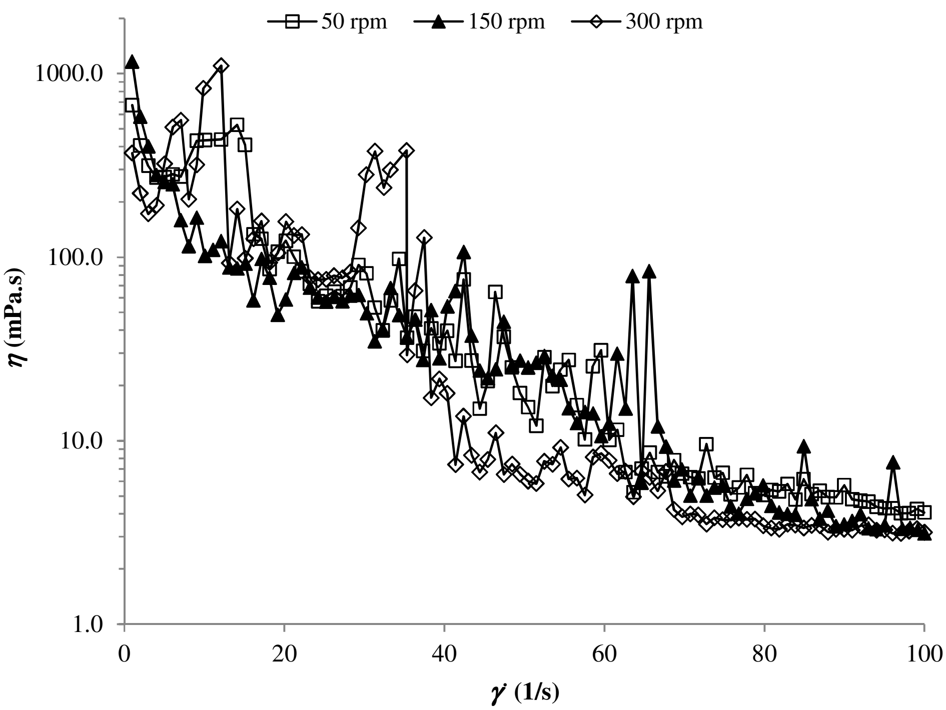

Figure B.8 Viscosity-shear rate curves of conditioned sludge at different mixing speeds

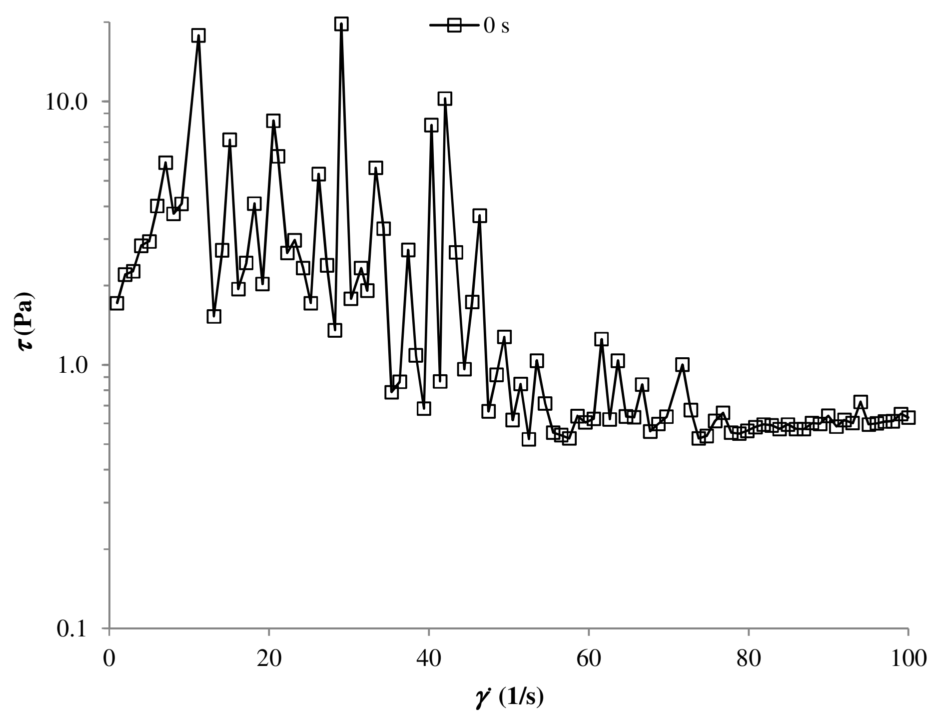

Figure B.9 Rheograms of conditioned sludge at the mixing time of 0 s

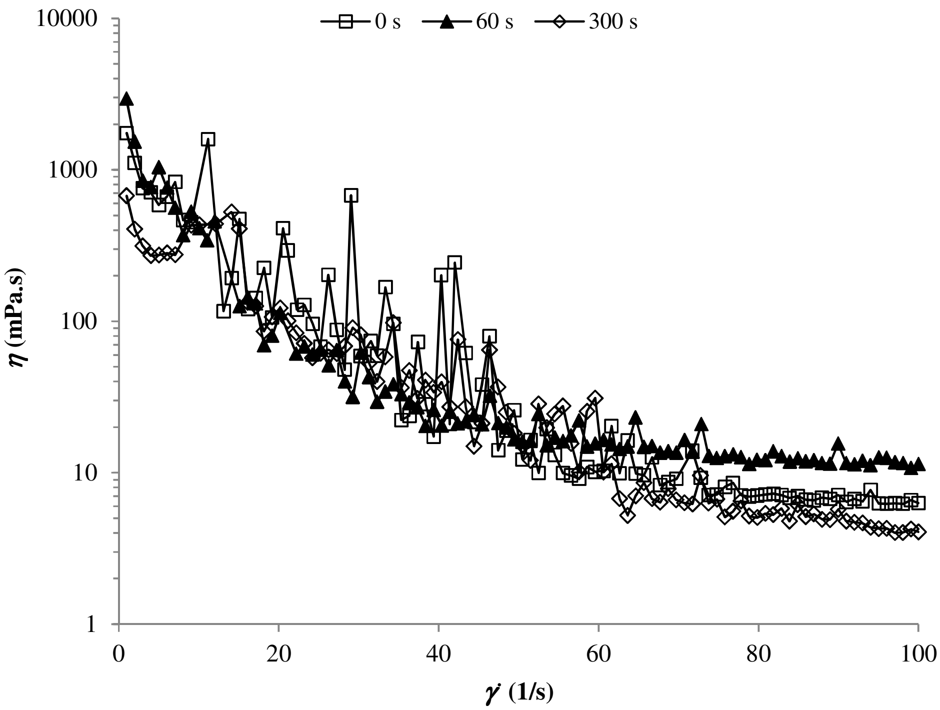

Figure B.10 Viscosity-shear rate curves of conditioned sludge at different mixing times