

# Sludge Treatment by Supercritical Water Oxidation and the Optimization of Operational Conditions

by  
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## **Executive summary**

The overall objective of this study was to investigate the performance of the supercritical water oxidation (SCWO) technology for the treatment of wastewater sludge, and investigate the degradation of p-tert-butylcatechol (TBC) which is a recalcitrant organic compound. The first phase of the study focused on the optimization of the thickening process that precedes SCWO, and investigated the impact of sludge temperature (10 °C -100 °C) on the optimum polymer dose and conditioning of wastewater sludge. The best results were observed at 35 °C -50 °C, where the highest filtrate volume, cake solids and settling velocity were obtained. The results showed that sludge conditioning at 35 °C -50 °C using the excess heat from the SCWO process can significantly improve treatment performance and result in savings for treatment plants. In the second phase, SCWO treatment of sludge was investigated under a range of operational conditions including sludge solids content (2-12 %), TBC concentration (0.1-1 %), reactor temperature (400-550 °C), reactor pressure (18-28 MPa), oxygen excess (n=1-8) and residence time (1-30 minutes). The results showed that the optimum initial sludge solids content was in the range of 8-10 %, and the optimum SCWO operational parameters were 550 °C, 25 MPa and an oxygen excess of 5. Addition of TBC decreased the percent COD removal but still 98% COD removal with final COD values less than 50 mg/L could be achieved. These results showed that SCWO is a very effective process for sludge treatment and degradation of recalcitrant organic compounds in sludge.

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## Nomenclature

A.R.	Analytical Reagents
atm	Atmosphere
cm	Centimeter
COD	Chemical oxygen demand
CST	Capillary suction time
DI water	Deionized water
$D_F$	Fractal dimensions
DS	Dry solids
EF	Electroflotation
EPS	Extracellular polymeric substances
Fig.	Figure
FT-IR	Fourier transform infrared spectroscopy
g	Gram
h	Hour
HPAC	High polymerized aluminum chloride
kPa	Kilopascal
KV	Kinetic viscosity
kW	Kilowatt
L	Liter
MPa	Mega Pascal
MBR	Membrane bioreactor
mg	Milligram
min	Minute
mL	Milliliter
N	Nitrogen
n	Oxygen excess

N/A	Not available
OH	Hydroxyl radical
PACl	Poly-aluminum chloride
PAM	Polyacrylamide
$p_c$	Critical pressure
PCBs	Polychlorinated biphenols
PS	Primary sludge
rpm	Revolutions per minute
RS	Raw sludge
S	Sulfur
SCWG	Supercritical water gasification
SCWO	Supercritical water oxidation
SCWPO	Supercritical water partial oxidation
sec.	Second
S.G.	Specific gravity
SMTD	Simultaneous thickening and digestion
SS	Suspended solids
SVI	Sludge volume index
TBC	p-tert-butylcatechol
$T_c$	Critical temperature
TS	Total solids
USD	US Dollar
V	Volt
WAS	Waste activated sludge
wt%	Weight percentage
WWTP	Wastewater treatment plant
°C	Degree Celsius

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# CHAPTER 1

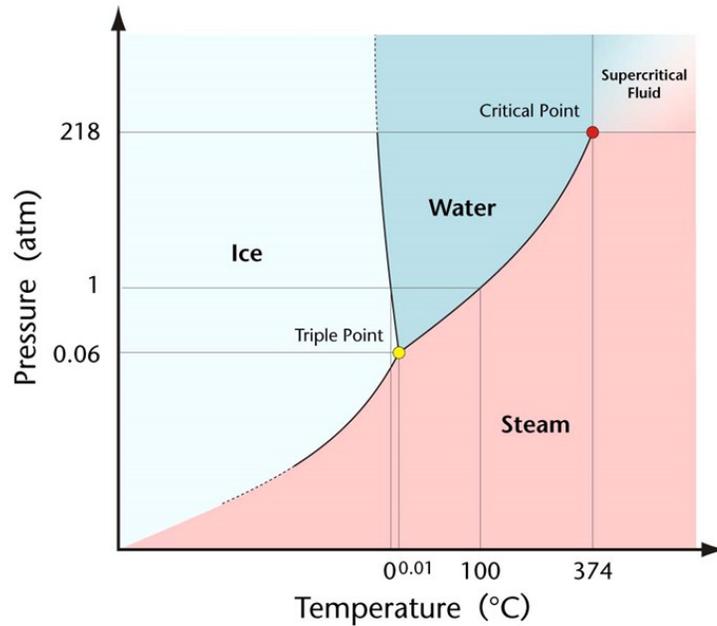
## 1 Introduction

Wastewater treatment is a growing challenge globally. The quantities of domestic and industrial wastewater continue to increase as new wastewater treatment facilities are built, and the existing ones are upgraded in order to keep up with population increase and strict regulations. Residuals that remain after wastewater treatment are called sludge, which includes solids as well as all other contaminants and pathogens present in wastewater in a concentrated form. Sludge still needs to be further treated and disposed of safely to prevent environmental pollution and minimize risks to public health. The high cost of wastewater and sludge treatment, the need for advanced treatment processes to achieve the removal of emerging contaminants and pathogens, and the strict limitations on discharge and disposal sites are forcing the wastewater industry to seek alternative technologies that can achieve complete destruction of chemical and biological contaminants.

Supercritical water oxidation (SCWO) has emerged as a viable technology in recent years for wastewater and sludge treatment offering many advantages such as the destruction of toxic organic compounds and pathogens, the elimination of odors, producing reusable end products such as clean water, carbon dioxide, minerals and metals, as well as the

generation of heat as a by-product of the process. The supercritical water is a state of the water where both pressure and temperature are higher than the critical point ( $T_c=374$  °C,  $p_c=22.1$  MPa, see Fig. 1.1). At this state, liquid and vapor coexist in equilibrium, and the water exhibits many unique properties, such as high diffusivity, low viscosity, controllable dielectric constant, reduced effect of hydrogen bonds and good heat-transporting properties (Zhang et al., 2016).

Pilot and small-full-scale SCWO systems for wastewater and sludge treatment have been employed in the USA, Japan, China, France and Sweden (Swanstrom, 2005; Sloan et al., 2009; Xu et al., 2012; Marrone, 2013), and there are several companies now who are actively working on the commercialization of SCWO systems and designing solutions to operational problems faced. SCWO can be used for the treatment of both domestic and industrial sludges. SCWO offers advantages particularly for the treatment of sludges that are contaminated with emerging organic contaminants, toxic compounds, and heavy metals.



**Fig. 1-1** Phase diagram of water (Abeln et al., 2001)

The initial sludge solids content, temperature, pressure, oxygen excess and the residence time are the operational conditions which need to be optimized to minimize the energy consumption of the SCWO and maximize the removal of the organic compounds at the same time. Temperature, pressure, oxygen excess and reaction time can be controlled in the SCWO reactor, and the solids content of the incoming sludge needs to be optimized before the SCWO. Water is required for the SCWO process. However, too much water would decrease the efficiency of the process by trapping a large amount of heat, and there also needs to be enough solids in the feed for feasible heat generation and recovery. Therefore, thickening and dewatering of sludge would be needed before SCWO is employed.

This study was carried out in two phases.

1. The objective of the first phase was to investigate the impact of sludge temperature on the optimum polymer dose and conditioning of wastewater sludge and improve the performance of settling, thickening and dewatering processes by using the optimum sludge temperature required for conditioning. The sludge temperature range selected for the study included temperatures of 10 °C -100 °C that can be employed at wastewater treatment plants in non-pressurized systems. In the temperature range of 10 °C to 50 °C, the polymer dose required for conditioning was similar but resulted in different thickening and dewatering performance. The best results were observed at 35 °C -50 °C, where the highest filtrate volume, cake solids, and settling velocity were obtained. Increasing the sludge temperature further to 60 °C and 100 °C increased the polymer demand and deteriorated the thickening and dewatering performance. These results showed that sludge conditioning at 35 °C -50 °C can significantly improve treatment performance and result in savings for treatment plants. There would be no additional cost for heating sludge at wastewater treatment plants where thermal treatment processes (e.g., SCWO) are used, and a step-wise temperature increase before thickening or dewatering can be easily incorporated using the heat recovered from the thermal process.

Results from the first phase of the study were published as:

Yan, Z., Ormeci, B.\* and Zhang J. (2016) Effect of sludge conditioning temperature on

the thickening and dewatering performance of polymers. *Journal of Residual Science and Technology*, Vol. 13, No. 3, 215-224. This manuscript is presented in Chapter 4 of this thesis.

2. The objective of the second phase was to determine the performance of the SCWO treatment for wastewater sludge, and investigate the degradation of p-tert-butylcatechol (TBC) under a range of operational conditions including sludge solids content (2-12 %), TBC concentration (0.1-1 %), reactor temperature (400-550 °C), reactor pressure (18-28 MPa), oxygen excess (n=1-8) and residence time (1-30 minutes). The results showed that the optimum initial sludge solid content was in the range of 8-10 %, and the optimum operational parameters were 550 °C, 25 MPa and an oxygen excess of 5. The addition of TBC decreased the percent COD removal but still 98% COD removal with final COD values less than 50 mg/L could be achieved. The results indicated that sludge treated with SCWO can be safely discharged to the environment without causing any concerns for public health or the environment.

## **1.2 Organizations of the thesis**

This thesis is written in the paper format and the chapters are organized as follows.

Chapter 1. Introduction

Chapter 2. Literature review

Chapter 3. Materials and methods

Chapter 4. Effect of sludge conditioning temperature on the thickening and dewatering performance of polymers (Manuscript #1)

Chapter 5. Supercritical water oxidation for treatment of wastewater sludge and p-tert-butylcatechol (TBC) (Manuscript #2)

Chapter 6. Conclusions

Chapter 7. Future work

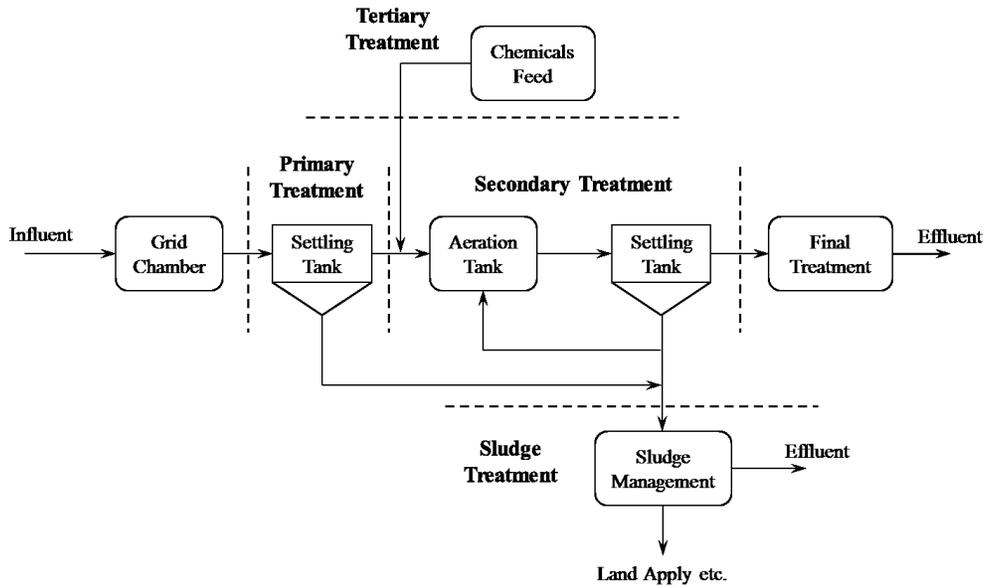
# **CHAPTER 2**

## **2 Literature Review**

### **2.1 Introduction to sludge management**

Sludge treatment and management continue to be a challenge for wastewater treatment plants. The goal of sludge treatment is to reduce the volume of sludge and achieve a final product that does not pose a risk to public health and the environment. Sludge is produced during preliminary treatment, primary treatment, secondary treatment and advanced treatment of wastewater, and is a good source of organic matter and nutrients that can be recovered and reused (Spinosa and Vesilind, 2001). However, a variety of harmful substances exists in sludge as well, including synthetic organic compounds, heavy metals, and pathogens.

The overall process of wastewater and sludge treatment is presented in Fig. 2-1 and Fig. 2-2.



**Fig. 2-1** General flow diagram of wastewater treatment processes



**Fig. 2-2** General flow diagram of conventional sludge treatment

Thickening, stabilization and dewatering play an important role in sludge minimization. During thickening, the water content can be reduced from 99% to around 95% or lower. After thickening, the total sludge volume can be decreased by 2/3. Physical and mechanical methods are typically used for thickening (e.g., gravity thickening, flotation, filtration and centrifugation). The goal of stabilization is to treat sludge so that it can be safely disposed of in the environment. Stabilization can be mainly achieved not only via aerobic and anaerobic digestion but also through other physical, chemical, and biological processes. During dewatering, excess water in sludge is removed where physical, chemical and mechanical processes can be selected and a soft cake is formed with a

typical water content of 85% - 70%. Polymers and other conditioners are added before dewatering to quickly release free water from sludge. Disposal is the final step in sludge treatment, and it is also very costly due to the handling, transportation, and disposal costs. The most commonly used disposal methods for municipal sludge are land application, landfilling and incineration (Spinosa and Vesilind, 2001). New generation thermal treatment processes are gaining popularity in recent years which are highly-efficient and environmentally-clean. Some of the main advantages of thermal treatment processes include drastic volume reduction, pathogen kill, phosphorus recovery, energy generation and no odour related issues. Supercritical water oxidation (SCWO) is an emerging thermal process and will be investigated in this study.

## **2.2 Pretreatment of sludge before SCWO**

The supercritical water oxidation is selected as the main research topic in this study and will be discussed in detail in section 2.3. Considering the high energy needs of the SCWO process due to the high temperature and pressure requirements, heat and material recovery are necessary to make the process feasible. The heat capacity of water is high, and water will absorb high quantities of heat. In an SCWO process, the heat is desired to be used for the degradation of sludge particles but not absorption by water. Therefore, the percentage of solids in sludge is an important factor that determines the heat generation and recovery. On the other hand, some water is needed for the SCWO process to proceed,

so too high solids may not be desirable either. If sludge is too thick, that could also adversely impact the pumping and piping of sludge in an SCWO facility. As a result, employing a combination of conditioning and thickening processes are needed before the SCWO process, and this section presents an overview of the science and applications on sludge thickening and dewatering.

### **2.2.1 Sludge thickening**

Thickening is the first step of sludge treatment that achieves volume reduction by removing some of the free water and increasing the solids content of sludge. Up to 12-15% of solids can be achieved after thickening if filtration or centrifuge based devices are used, and gravity thickeners can thicken sludge typically up to 6-8% solids. Thickening results in major savings to treatment plants by reducing the reactor volumes that come later in the treatment and increasing treatment performance by increasing the concentration of sludge solids. Gravity thickeners are the simplest and most cost-effective method of thickening, and they achieve thickening through the settling of sludge particles and use of polymers and other inorganic conditioners.

When the density of sludge is in the range of 1.004~1.008, and the particle density is in the range of 1.3~1.4, gravity thickening is typically chosen since it works well and it does

not require energy, unlike mechanical thickeners. Particle size and density, as well as the operational parameters of the gravity thickeners, determine the final solids concentration of thickened sludge. Spinosa and Vesilind (2001) summarized the advantages and disadvantages of gravity thickeners as follows: *a*) thickeners can deal with a wide range of inlet solids and flux range; *b*) thickening can reduce water content in the sludge at a low operational cost. The disadvantages include: *a*) thickeners are poorly suited to producing very high solids underflows from materials with a specific gravity close to unity; *b*) the efficient operation of a thickener is highly dependent on the maintenance of the solids bed, the height of which can fluctuate wildly in high flux conditions; *c*) the underflow solids is often limited by the torque capacity of rakes used to move the solids to the underflow discharge point; *d*) stable zones of operation in terms of overflow and underflow flux are often ill-defined and operator-sensitive.

Several empirical and theoretical models were developed for primary and secondary sludges to better design the gravity thickeners, determine the thickener performance, and optimize the operational parameters (Takacs et al., 1991, Giokas and Kim et al., 2002, Spehar and Kiviti-Manor et al., 2015, Grassia and Zhang et al., 2014). An easily measured index of sludge settlability is the sludge volume index (SVI) which can be correlated to the settling behavior of sludge and gravity thickener performance (Koopman and Cadee, 1983).

Centrifuges are commonly used for sludge thickening and dewatering. The performance of a centrifuge is mainly determined by the type of sludge, type of centrifuge, feed rate, polymer dose, scroll torque, and retention time. Centrifugation process can be divided into three parts: clarification or removal of solids from the liquid, consolidation of the solids, and conveyance of solids to the discharge point. Dewatering with advanced centrifuges was shown to reduce the operating costs (chemicals, personnel, power, capital servicing, transportation and landfilling) of sludge at least by 20%. Improved thickening of waste activated sludge can produce savings of 20-80% in the treatment and disposal cost of dewatered sludge (Retter and Schilp, 1993).

When the density of sludge is close to 1.0, the gravity settling will not work well, but flotation thickening would be suitable during flotation, sludge particles are floated up typically through the generation of bubbles in pressurized systems and thickened sludge is collected from the surface. During flotation thickening, some flocculants, i.e. aluminum salts, ferrous/ferric salts, activated silica, polymer electrolytes (such as polyacrylamide, PAM) etc. can be added. The properties of the bubble-liquid surface and solid-liquid surface are enhanced via the additives, which increases the flotation performance. In addition, flotation performance can be improved by optimization of the bubble formation and bubble size distribution (Rijk et al., 1993). Generally, after the flotation thickening the water content could be reduced from 99% (or higher) to 95-97%.

New technologies have started using membrane processes (e.g., flat-sheet membranes, hollow fiber membranes) for sludge thickening, and some combine thickening with digestion such as the simultaneous thickening and digestion (SMTD) process (Wang et al., 2008; Zsirai et al., 2014). Membranes are very effective and they allow a better control on the particle size and concentration allowing a much thicker sludge. Despite their effectiveness, membrane based processes encounter operational challenges mainly due to the fouling of the membranes. They are also substantially more expensive in capital and operational costs compared to the other thickening processes.

Electro-thickening is another new technology that is now used in full-scale treatment plants such as the Gagnon Wastewater Treatment Plant (WWTP) in Victoriaville, Quebec (National Biosolid Partnership, 2012). Electro-thickening is a modification of flotation thickening, and uses oxygen and hydrogen gases generated from water electrolysis for bubbles. The main advantage of the electro-thickening process is the smaller size of the bubbles compared to the conventional flotation technologies, and better control of the process by controlling the current density (Cho et al., 2010, Rahmani et al., 2013). Continuous thickening of activated sludge by electro-flotation has been investigated. Initial pH, current density, operating time, electrode type (stainless steel and graphite) and operational conditions are the main parameters that affect the performance and feasibility of electro-thickening (Rahmani et al., 2013).

### **2.2.2 Sludge Conditioning**

Wastewater sludge mainly consists of charged organic particles and require physical or chemical steps to reduce the magnitude of the repulsive forces, break down the collidal structure and achieve the separation of particles. Physical processes typically utilize temperature (e.g. freezing) and chemical processes use chemical additives such as organic polymers and inorganic conditioners (ferric chloride, alum, etc.). Both physical and chemical processes alter the microstructure of the sludge and achieve coagulation and flocculation followed by the separation of particles.

Chemical conditioning is the most widely used method of conditioning due to its ease and effectiveness, and involves using coagulants, coagulants aids, and precipitants. For sludge treatment, high molecular-weight organic polymers (anoionc or cationic) and inorganic conditioners (lime and ferric salts) are used. The role of the coagulant aids is to change the sludge pH, modify the sludge matrix, and enhance the performance of coagulants. Coagulant aids may include diatomite, clay, and coal ash which are porous materials.

The mechanisms of action for synthetic polymers and inorganic conditioners are very different. Synthetic polymers achieve coagulation and flocculation through particle charge neutralization and polymer bridging. Inorganic conditioners, on the other hand,

achieve coagulation and flocculation through dissociation, hydrolysis, nucleation and precipitation. The nucleation happens on the surface of the sludge particles and ferric hydroxide precipitates form on the particle surfaces during this process leading to the charge neutralization. There is also a decrease in pH because of the hydrogen ions generated during hydrolysis. Aluminum salts have similar mechanisms of action with ferric or ferrous salts, and the patch model is appropriate for the inorganic conditioners.

However, there are two major disadvantages of ferric/ferrous salts and lime. *a)* Their performance is lower compared to organic polymers and they may cause corrosion problems and equipment wear due to the pH changes. *b)* Compared with organic additives, the dry content of sludge will sharply increase by a factor of 20-40% due to the formation of chemical sludge. Such large increases in sludge quantities and volume substantially increase the cost of sludge treatment, handling and disposal for wastewater treatment plants.

The conditioning of aluminum-based water treatment sludge with Fenton's reagents ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) and its effectiveness on sludge thickening was investigated by Tony et al. (2008). Fenton reaction could split the macromolecules into small size particles rapidly. By optimizing the quantities of  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ , pH, etc., the capillary suction time (CST) was reduced by 53% under the optimized conditions of  $\text{Fe}^{2+} = 21 \text{ mg g}^{-1} \text{ DS}^{-1}$ ,  $\text{H}_2\text{O}_2 = 105 \text{ mg}$

$\text{g}^{-1} \text{DS}^{-1}$  and  $\text{pH} = 6$ . The joint application of Fenton reagent and CaO on sewage sludge was studied by Liu et al., 2014, and similar improvements were reported. The process increased the porous structure of the bulk sludge and suppressed the emission of S- and N-containing gasses and odors were suppressed considerably during the sludge thickening after using the mixed Fenton reagent and CaO.

The changes on the physicochemical properties of sludge after using inorganic coagulants  $\text{FeCl}_3$ , PACl, and HPAC were investigated by Niu et al. (2013). They used  $\text{FeCl}_3$ , PACl, and HPAC as a conditioner and measured the changes in the particle size, kinetic viscosity (KV), fractal dimension ( $D_F$ ) and extracellular polymeric substances (EPS). The EPS content was shown to be closely related to the improvements in sludge thickening. Christopher et al. (2014) compared the two types of inorganic polymer flocculants, PACl and HPAC, and reported that the HPAC was a much more effective conditioner compared to the PACl due to its high charge density and better bridging properties.

Maximizing the polymer efficiency and minimizing the polymer use is an effective way to reduce the operational cost of sludge conditioning and dewatering. In addition, several parameters can be optimized including operational parameters, environmental conditions, polymer type and chemistry, and sludge characteristics which are reviewed below.

To minimize the polymer use, the mixing regime used during conditioning was tested by Werle et al (1984) including a variable speed mixer with root mean square velocity gradient values in the range of 250-2000  $\text{sec}^{-1}$ . Both anionic and cationic high molecular weight polymers were tested in the speed mixers. As a result, the performance of high-stress conditioning was significantly influenced by the total mixing energy input ( $Gt$ ). Novak and Lynch (1990) also studied the relationship between the mixing energy input and the performance of the sludge conditioning. After conditioning, the treated sludge was characterized through CST and filtration test and it was reported that the filtering results were related to the mixing energy input.

Shear exposure after conditioning was reported as another factor which can affect the polymer use (Örmeci and Ahmad, 2009). It was proved that the cake solids concentration performed decreasingly with more shear exposure after conditioning. As a result, a linear relationship emerged between the applied shear and the torque, which can be applied in the sludge condition rheological analysis.

Importance of choosing the right polymer type and chemistry based on sludge characteristics was reported by Murray and Örmeci (2008). Wastewater particles are negatively charged and thus cationic polymers with positive charge are the most commonly used organic polymers for wastewater and sludge treatment. Polyacrylamide

(PAM) and acrylamide (AM or ACM), AMPAM (aminomethylated polyacrylamide), DMAEMA (dimethylaminoethyl methacrylate), DMAEA (dimethylaminoethyl acrylate), MAPTAC (methacrylamidopropyltrimethylammonium chloride), and DADMAC (diallyldimethyl ammonium chloride) are some of the main monomers used in polymers (Vesilind, 2001). Polymers can be linear or branched, and branched polymers have a three dimensional structure and typically perform better.

Sludge characteristics also play an important role in determining the dewatering performance. pH was reported as one of the factors that affect dewatering and pH adjustment as a pretreatment step was recommended (Amuda and Amoo, 2007). The cations in sludge can affect the polymer dose required, and it was reported that the lower the concentration of the cations in sludge, the higher the polymer dose that was required (Park et al., 2006). Zhao (2003) studied the relationship between the polymer dose and physical properties of flocs such as the size, density, and structure. Increasing the polymer dose increased the size and fractal dimension of the flocs. Increases in floc density also correlated well with the increasing polymer dose.

It has been known that cold temperatures are not ideal for conditioning, but there have not been extensive studies on the effect of sludge temperature on sludge conditioning, thickening, and dewatering. Polymers are typically dosed at room temperature; however,

wastewater and sludge temperatures may vary largely based on the seasonal variations and the treatment processes used at treatment plants.

## **2.3 Supercritical water oxidation (SCWO)**

### **2.3.1 Rationale for supercritical water oxidation**

The conventional approaches of wastewater and sludge treatment face the challenges of complex economic and social requirements and increasingly strict emission standards. Supercritical water oxidation achieves safe, rapid and efficient treatment of wastewater and sludge. A wide range of pollutants (e.g., polychlorinated biphenyls (PCBs), pesticides, cyanide, etc.) can be treated by the SCWO and complete degradation can be achieved.

As shown in Fig. 1-1 in Chapter 1, when water reaches the critical point ( $T_c=374$  °C,  $p_c=22.1$  MPa), it enters the supercritical state. Around the critical point, a small pressure alteration can lead to a big change in the property of water. At supercritical state, the density of water is close to that of the liquid water and the mass transfer property is close to that of the water vapor. Therefore, SCWO offers many advantages in waste treatment because of the liquid-like solvent property and the gas-like mass transfer property of the supercritical water.

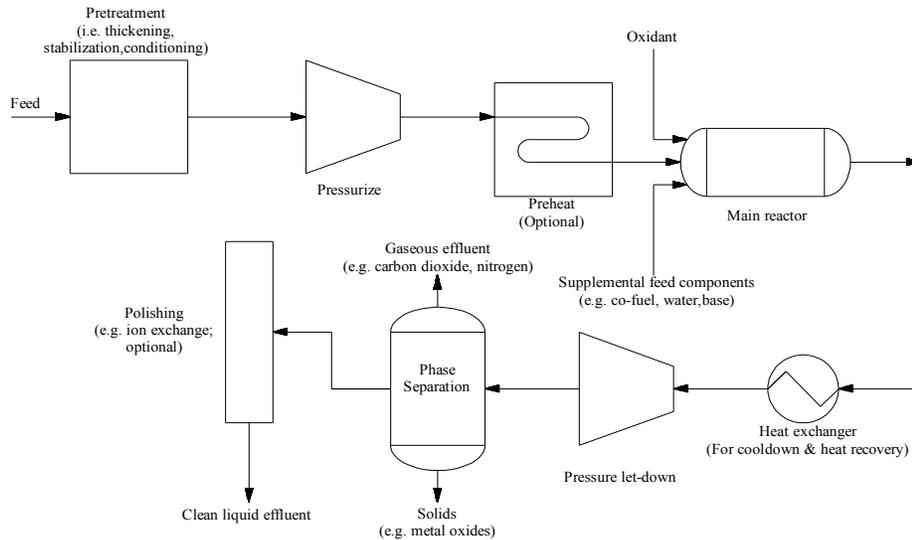
When temperature and pressure cross the critical point, the density of water decreases in one order of magnitude. The number of hydrogen bonds decreases from 3.5 per molecule (stoichiometrically 4 per molecule) to 1.8 per molecule, which decreases the molecular interactions. The dipole moments of water will be eliminated, and the water molecules behave as non-polar. Therefore, the non-polar (weak polar) organic compounds and the oxidants can be solved in supercritical water, and a homogenous system can be generated.

The reaction of SCWO is to mix the pollutants into a water-rich system with the oxidants above the conditions of the critical point of water. At that high temperature and pressure, the organics can be fully degraded into small molecules, namely, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and inorganic mineral acids. If the system is treated by alkali, the materials remaining will be carbonates, H<sub>2</sub>O, N<sub>2</sub> and inorganic salts. These salts and carbonates can be filtered and the gasses (water vapor and N<sub>2</sub>) can be directly discharged into the atmosphere. The SCWO of organics can be presented as below:



For the SCWO process, the viscosity and solids content cannot be too high to hinder pumping of the feed into the SCWO reactors. The preheating of the feed is sometimes used because of the high reactor temperature of the SCWO, and the preheating step may

help to cut down the capital cost of the reactors. In full-scale SCWO processes, heat recovery and the materials separation are required for both the economic and environmental reasons. Therefore, the heat exchanger system, pressure let-down system, and separation systems are commonly installed after the SCWO reactor. A general flow diagram of the SCWO process is summarized in Fig. 2-5.



**Fig. 2-3** General flow diagram of SCWO process (Kutz, 2007)

### 2.3.2 Current applications of SCWO

SCWO has had a rapid development in recent decades worldwide and has been used in the fields of wastewater/sludge treatment, military industry, nuclear industry, etc. Fig. 2-6 summarizes the main pilot-scale and full-scale plants worldwide (Marrone et al., 2005; Grumett, 2003; Oe et al., 1998; Jayaweera, 2003; Svensson, 1995; Griffith et al., 2001;

Yan et al., 2016).

According to Fig. 2-6, the tank, and tubular reactors are the two main types of the SCWO reactors. The tubular reactor is beneficial for continuous treatment. The daily capacity of the tubular reactor can achieve 150 tons per day while the tank reactor can achieve 105 tons per day per reactor. A feasibility analysis of the SCWO facility of the CEAB Corp. (tubular reactor, O<sub>2</sub> as the oxidant, 7% initial sludge solids concentration) showed that the operational cost can be steadily controlled at 21 USD per ton, which is lower than some of the conventional approaches such as incineration.

However, some of the SCWO facilities shown in Fig. 2-6 were shut down after a period. For example, the SCWO of CEAB of Sweden sold the facility to a company in Ireland because of the high energy consumption and insufficient heat recovery. Also, HydroProcessing's SCWO facility in Harlingen was shut down only after one year because of the problems faced with the corrosion of the materials. Many research studies have focused on these operational problems in recent years. Wang et al. (2012) have designed and run a pilot-scale SCWO reactor for treatment of sewage/industrial sludge and partially solved the problems of metal corrosion, pipeline fouling, and high investment. In addition, ENN Group in China has been successfully running 4 types of SCWO reactors for wastewater and sludge treatment since 2008.

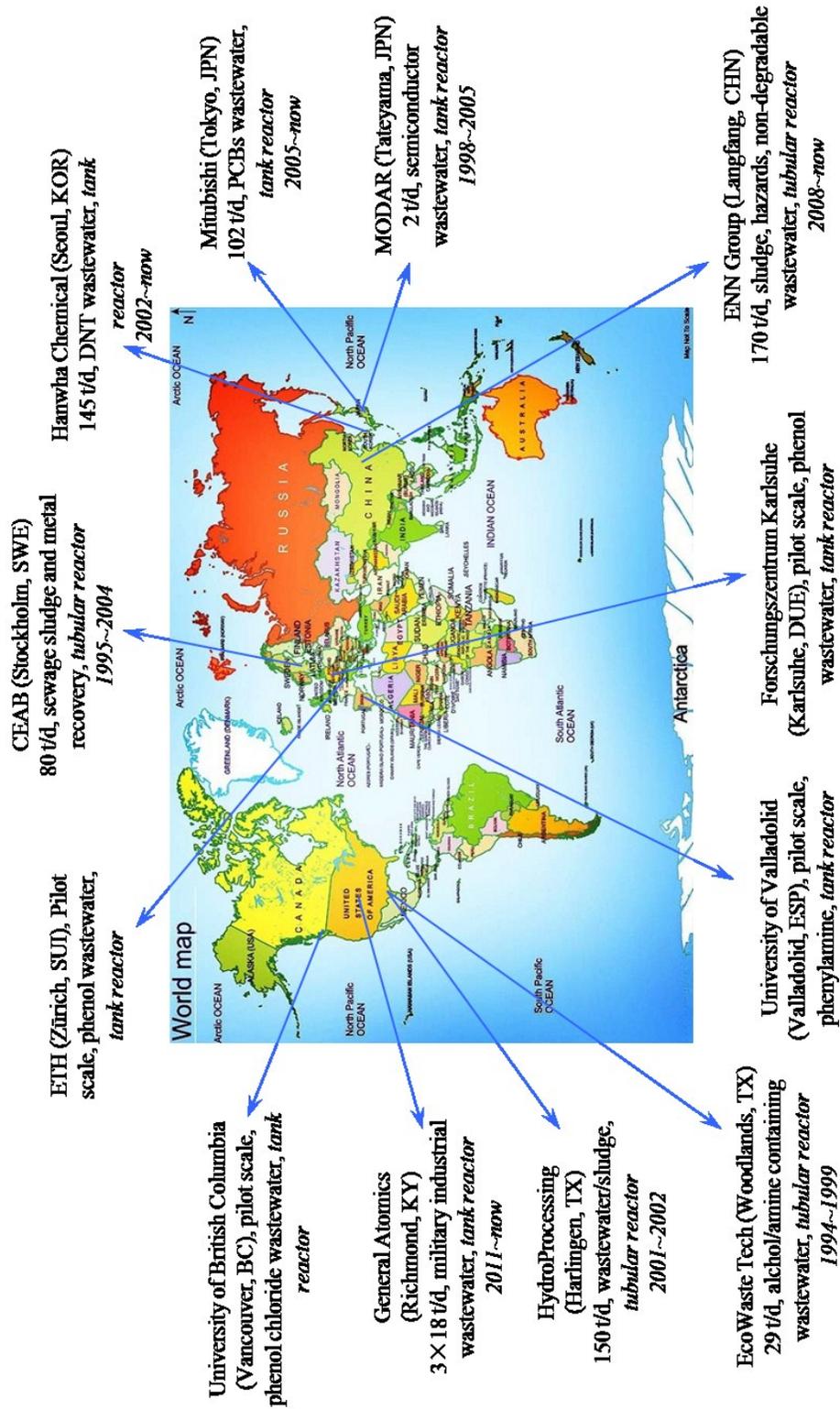


Fig. 2-4 Application cases of SCWO worldwide

### **2.3.3 SCWO treatment of phenol-contaminated wastewater/sludge**

The high density of delocalized electrons in phenol leads to high molecular stability, which makes the opening of the aromatic ring difficult. Supercritical water oxidation has shown superior performance for the degradation of phenol in wastewater and sludge. The solubility of phenol sharply increases because the polarity of water molecules decrease when water achieves the supercritical state. Therefore, the oxidants and the water dissolve in a homogenous aqueous system. If hydrogen peroxide is chosen to be the oxidant for the SCWO, the activated OH radical can initialize the radical reaction of phenol. Gopalan et al. (1994) reported the ring opening mechanisms of phenol. The phenol molecules react with the OH radicals and form the phenol radicals. Then the phenol radical combines with another OH radical and forms the oxidized phenol radical. The rearrangement reaction emerges on the oxidized phenol radical which causes the opening of the aromatic ring and formation of the carbon chains correspondingly. The OH radical then oxidizes the carbon chains, which are easier to be degraded, compared to the aromatic rings. Fourcault et al. (2009) and Thronton et al. (1991; 1992) modeled the radical ring opening mechanisms and partially proved the mechanisms experimentally.

The great majority of the SCWO processes have been studied in lab-scale. However, there have been some pilot-scale studies on the treatment of phenol contaminated wastewater and sludge including ENN Group (Yan et al., 2016), Forschungszentrum

Karlsruhe (Abeln et al., 2001), ETH (Wellig et al., 2005), University of British Columbia (Teshima et al., 1997) and University of Valladolid (Cocero et al., 2000). According to the scale-up studies listed above, phenol, phenol chloride, DDT, biphenyl benzene and the derivatives can be fully broken down and degraded in the supercritical water systems. Also, the ENN Group is planning to apply the SCWO technology for the treatment of coking wastewater/sludge (contains p-tert-butylcatechol, TBC) with a daily capacity of 170 tons.

## **CHAPTER 3**

### **3 Materials and Methods**

This chapter presents the materials, methods, and procedures used in this study in one chapter. The thesis is written in the paper format, and Chapters 4 and 5 have their individual materials and methods sections.

### 3.1 Materials and chemical reagents

All the raw materials and chemical reagents used in this study are listed in Table 3-1.

**Table 3-1** Materials and chemical reagents

Name	Chemical Formula	Standard and Purity	Manufacturers
Anaerobically digested sludge (1)	N/A	N/A	ROPEC, Ottawa, ON, Canada
Anaerobically digested sludge (2)	N/A	N/A	Beichen Wastewater Treatment Plant, Tianjin, China
Zetag 8160	N/A	N/A	BASF
Phenol	C <sub>6</sub> H <sub>5</sub> OH	A.R.	Kermel Chemical Reagent Co., Ltd, Tianjin, China
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	A.R.	Guangfu Fine Chemical Research Institute, Tianjin, China
p-tert-butylcatechol	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	A.R.	Aladdin Industrial Corporation, Shanghai, China
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	30%	Jingtian Industry Co., Ltd, Tianjin, China
Methanol	CH <sub>3</sub> OH	A.R.	Kermel Chemical Reagent Co., Ltd, Tianjin, China
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	A.R.	Kermel Chemical Reagent Co., Ltd, Tianjin, China
DI Water	H <sub>2</sub> O	N/A	Prepared in the lab
Nitrogen	N <sub>2</sub>	≥99.999%	Liufang Industrial Gas Co., Ltd, Tianjin, China
Oxygen	O <sub>2</sub>	≥99.99%	Liufang Industrial Gas Co., Ltd, Tianjin, China
COD kit (1)	N/A	Test range: 20~1500 mg/L	Hach Co., Loveland, US
COD kit (2)	N/A	Test range: 3~150 mg/L	Hach Co., Loveland, US

It should be mentioned that two kinds of anaerobically digested sludge collected from two different wastewater treatment plants (WWTP) were used. Anaerobically digested sludge (1), which was used in the first phase of the study, was picked up from ROPEC in

Ottawa, Ontario, Canada. Anaerobically digested sludge (2), which was used in the second phase of the study, was picked up from Beichen WWTP in Tianjin, China. The total solids (TS) of the two anaerobically digested sludges were 2.4 wt% and 5.2 wt%, respectively. Zetag 8160, a polyacrylamide based high molecular weight and medium cationic charge polymer, was used as the conditioner in the first phase of the study.

### 3.2 Methodology for Phase I (Chapter 4)

The summary of equipment and the instruments used in *Phase I* are listed in Table 3-2.

**Table 3-2** Equipments and instruments in *Phase I*

Equipments/Instruments	Type	Manufacturer
Jar tester	PB-700 Jartester	Phipps & Bird Inc., USA
CST tester	Type 319 Multi-CST	Triton Electronics Ltd., England
Zeta meter	Zeta-Meter System 4.0	GENEQ Inc.

#### 3.2.1 Preparation of sludge samples

Anaerobically digested sludge samples were collected from ROPEC, Ottawa, Ontario, Canada once a week. The plant digests mixed primary and secondary sludge under mesophilic temperatures. Sludge samples were stored in a refrigerator, and samples were brought to room temperature before use. A hot plate was used to increase the temperature of samples to 10 °C, 35 °C, 50 °C, 60 °C, and 100 °C in 2 L glass beakers while being stirred at 200 rpm. After reaching the target temperature, sludge samples were conditioned with a polymer as explained below.

### **3.2.2 Preparation of polymer stock solution**

The polymer used in this study was Zetag 8160 (BASF), which is a polyacrylamide (PAM) with a specific polymerization degree, a medium-high cationic charge that is in granular solid form. The polymer stock solution was prepared at a concentration of 0.5 wt% using a jar tester (PB-700 Jar tester, Phipps & Bird Inc., USA). 5 g of Zetag 8160 polymer was mixed with 1 L of deionized water and stirred for first 5 min at 200 rpm followed by 55 min at 125 rpm. A hand-held blender was used to break up the remaining polymer clumps, and the solution was left for 24 hours maturation.

### **3.2.3 Conditioning of sludge samples**

Sludge samples of 200 mL were spiked with polymer and conditioned in 500 mL beakers using a jar tester apparatus (PB-700 Jar tester, Phipps & Bird Inc., USA). Polymer doses were selected to cover the under-dose, optimum dose and over-dose polymer ranges. The polymer was rapidly injected into the sludge samples, and mixed at 200 rpm for 2 min and 30 sec. After conditioning, sludge samples were used for the settling, filtration, capillary suction time (CST) and zeta potential tests as explained below. All experiments were run in triplicate, and the average values are shown in the figures. Polymer doses are reported as g/kg DS (dry solids).

### **3.2.4 Evaluation of thickening and dewatering performance**

#### **3.2.4.1 Capillary suction time (CST) test**

Capillary suction time (CST) test was used to evaluate the dewaterability of sludge samples after conditioning with the polymer. A CST tester (Type 319 Multi-CST, Triton Electronics Ltd., England) was used with the CST paper (No. 17 chromatography grade paper cut into 7- × 9- cm, Whatman PLC), and the protocol outlined in the Standard Methods (APHA, 2005) was followed.

#### **3.2.4.2 Filtration test**

Conditioned sludge samples of 200 mL were filtered for 3 minutes using 55 mm-diameter coarse filters (Fisher Scientific Ltd.) and a vacuum pump. Filtrate volume and total solids concentration of the cake remaining on the filter were measured after filtration. The total solids concentration of the cake was determined following the protocol in the Standard Methods (APHA, 2005).

#### **3.2.4.3 Zeta potential test**

After the filtration tests, 10 mL of the filtrate from each sample was used for measuring the zeta potential. The filtrate samples were diluted by 10 times, and 10 particles were tracked to get the average zeta potential for each sample. Zeta potential measurements

were performed using a zeta meter (Zeta-Meter System 4.0, GENEQ Inc.) operated at the default cell parameters of 200 V and 25 °C. Samples that were conditioned and dewatered at higher temperatures were cooled down to 25 °C before the zeta potential measurements.

#### **3.2.4.4 Settling test**

Settling tests were carried out in 100 mL graduated cylinders in triplicates. 100 mL of the conditioned sludge sample was transferred to each graduated cylinder, and the height of the interface between the solid and the liquid phases was recorded for 30 minutes. The final height of the interface indicates the settling and thickening performance of the conditioned sludge. After the settling curves had been established, the slopes of the lines before the inflection point (first 60 seconds) were used to calculate the settling velocities.

### 3.3 Methodology for Phase II (Chapter 5)

The summary of equipment and the instruments used in *Phase I* are listed in Table 3-3.

**Table 3-3** Equipments and instruments in *Phase II*

Equipments/Instruments	Type	Manufacturer
Supercritical reaction vessel	CXF-05	Runchang Petrochemical Equipment Co., Ltd, Dalian, China
COD digester	DRB 200	HACH Co., Loveland, US
COD Spectrometer	DR 1010	HACH Co., Loveland, US
FT-IR	NICOLET iS10	Thermo Scientific, US
Electric conductivity meter	DDS-307	Electronic Scientific Co., Ltd, Shanghai, China
pH meter	pH 211 Microprocessor	HANNA Instrument, Limena, Italy

#### 3.3.1 Sludge samples

The anaerobically digested sludge was obtained from the Beichen Wastewater Treatment Plant (Tianjin, China). The total solids content of the sludge sample after drying at 105 °C for 24 h was measured as 5.2 % (wt). For the SCWO experiments, sludge samples with solids concentrations of 2, 4, 6, 8, 10, and 12 % (wt) were prepared by first drying the sludge in the oven and then adding deionized water (DI).

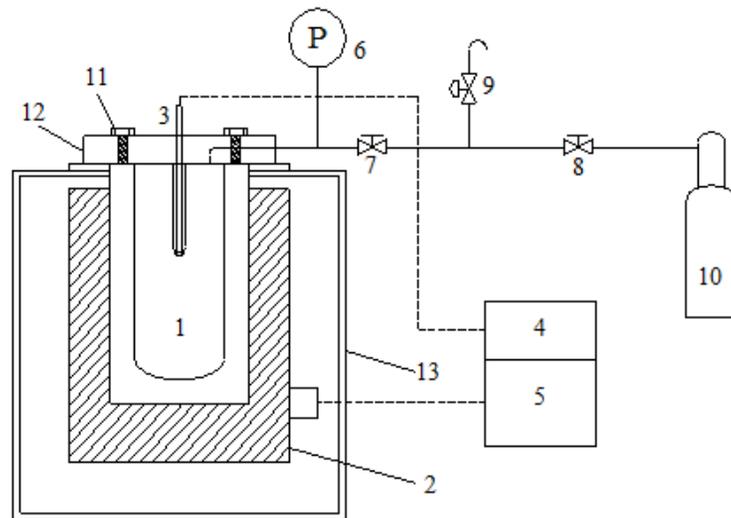
#### 3.3.2 Reagents

Hydrogen peroxide 30 % (w/w) (Jiangtian Industry Co., Ltd, Tianjin, China) was used as the oxidant for the SCWO process. The stock solution of the TBC was prepared by dissolving the chemical in the DI water to give a final concentration of 0.15 % (wt). TBC was then spiked in sludge samples to give the desired concentrations of 0.1, 0.5, and 1 %

(wt) before the SCWO treatment.

### 3.3.3. SCWO Reactor

A high-pressure and high-temperature reaction vessel (Runchang Petrochemical Equipment Co., Ltd, Dalian, China) was used in this study for the SCWO reaction (Fig. 2). The volume of the reactor is 0.5 L, the design maximum temperature is 650 °C, and the design maximum pressure is 30 MPa. The working temperature and pressure are recommended not to exceed 600 °C and 25 MPa, respectively. The total power of the heater is 2.5 kW. During the operation of the SCWO, 0.5 L sample volumes of sludge were used with different solids and TBC concentrations.



**Fig. 3-1** SCWO set-up– 1: Reaction Vessel; 2: Heater; 3: Thermal couple; 4: Thermal meter; 5: Thermal meter for the heater; 6: Pressure sensor and pressure indicator; 7, 8: Gate valves; 9: Air release valve (globe valve); 10: Nitrogen cylinder; 11: Screws; 12: Vessel cap; 13: Vessel bracket



**Fig. 3-2** SCWO set-up picture

### **3.3.4. Determination of treatment performance**

#### **3.3.4.1. Chemical Oxygen Demand (COD)**

Chemical Oxygen Demand (COD) test kits by HACH were used for measuring the initial and remaining (residual) COD in sludge, and the percent COD removal after SCWO treatment. The COD test is achieved via two steps that include sample digestion and measurement. A Digital Reactor Block (DRB) 200 was used for the digestion of the sludge samples. For COD analysis, 2 mL of the aqueous sludge sample was mixed with the COD reagents and digested at 150 °C and incubated for 2 h. A blank sample was prepared using 2 mL DI water and following the same procedure for the COD test. After cooling down the test tube contents, the tubes were placed into the HACH spectrophotometer cell, and the COD values were measured.

#### ***3.3.4.2. Fourier Transform Infrared Spectroscopy (FTIR)***

The degradation level of organic compounds in sludge samples before and after the SCWO treatment was measured using Fourier Transform Infrared Spectroscopy (FTIR) (NICOLET iS10, Thermo Scientific, US). FTIR provides an infrared spectrum of absorption or emission, and it is particularly effective on polymers and organic compounds. When a sample is exposed to infrared radiation (IR), some of the radiation is absorbed by interatomic bonds at varying intensities and at varying frequencies resulting the bonds to vibrate in different motions, such as stretching and bending. The resulting spectrum represents a fingerprint of the sample, and the peaks can be directly correlated to the bonds within the compound. The quantity of the OH groups, C-C and C=C bonds can be determined based on the stretching and vibration of these bonds. The stretching and vibration of the interatomic bonds change due to the splitting of the bonds in the carbon chains and the aromatic rings after the SCWO treatment. Therefore, the differences in the FTIR spectra before and after SCWO can be utilized to evaluate the extent of degradation of the organic compounds in sludge samples. The FTIR spectra were recorded using a Bruker Vertex 70 FTIR Spectrometer in the IR spectrum of 700~4500  $\text{cm}^{-1}$  with the resolution of 4  $\text{cm}^{-1}$ .

## **CHAPTER 4**

### **4 Effect of Sludge Conditioning Temperature on the Thickening and Dewatering Performance of Polymers**

#### **Abstract**

Water soluble polymers are one of the most expensive chemicals used during wastewater treatment. The objective of this study was to investigate the impact of sludge conditioning temperature on the optimum polymer dose, and thickening and dewatering performance of polymers used for wastewater treatment. Thickening and dewatering performance was investigated at 10 °C, 35 °C, 50 °C, 60 °C, and 100 °C using filtration test, capillary suction time (CST) tests, settling tests and zeta potential measurements. A high molecular weight and medium-high cationic charge polyacrylamide polymer (Zetag 8160) was used to condition sludge. Results showed that 50 °C was the sludge temperature that resulted in the best settling, thickening, and dewatering using the least amount of polymer, and 35 °C was also effective. The number of wastewater treatment plants employing thermal sludge treatment processes has rapidly increased in recent years, and a step-wise temperature increase can be used to increase the sludge temperature before conditioning. The results of this research indicate that such an approach would improve the performance of sludge thickening and dewatering at no additional cost.

## **Keywords**

Sludge, conditioning, thickening, dewatering, polymer, temperature

## **4.1 Introduction**

The cost of sludge management constitutes approximately half of the cost of wastewater treatment (Nowak, 2006), and the quantities continue to increase as new wastewater treatment plants are built, and the existing ones are upgraded to keep up with the growing population and stricter regulations. Sludge thickening and dewatering play a key role in reducing the treatment and final disposal costs at wastewater treatment plants. Cationic polymers are used for both thickening and dewatering processes, and the optimization of their use would substantially improve the performance of these processes. Both under-dosing and over-dosing lead to poor settling and dewatering, and therefore it is important to use polymers at the optimum dose (Al Momani and Örmeci, 2014). Moreover, polymers are one of the most expensive chemicals used for wastewater treatment, and using polymers at the optimum dose and under optimum conditions would help to achieve major savings for wastewater treatment plants.

To maximize the polymer efficiency and minimize the polymer use, several parameters can be optimized including operational parameters, sludge characteristics, and environmental conditions. These include mixing used during conditioning (Werle et al., 1984; Novak and Lynch, 1990), shear exposure after conditioning (Örmeci and Ahmad,

2009), polymer type and chemistry (Murray and Örmeci, 2008), pH (Amuda and Amoo, 2007), metal ions (Park et al., 2006), ionic effects (Shi et al, 2015; Zhang et al, 2012), extracellular polymers (Houghton and Stephenson, 2002) as well as sludge temperature. It has been known that cold temperatures are not ideal for conditioning, but there have not been extensive studies on the effect of sludge temperature on sludge conditioning, thickening, and dewatering. Polymers are typically dosed at room temperature; however, wastewater and sludge temperatures may vary largely based on the seasonal variations and the treatment processes used at treatment plants.

Heating sludge is very costly and therefore it is not typically used to improve conditioning unless heating is part of the treatment process. In recent years, there has been a major interest in the use of new and innovative thermal processes for sludge pre-treatment, treatment or dewatering. These processes include thermal and thermochemical hydrolysis (Neyens and Baeyens, 2003), incineration (Werther and Ogada, 1999), wet air oxidation (Bertanza et al., 2015), and super-critical water oxidation (Griffith and Raymond, 2002; Qian et al., 2015). The thermal processes require sludge temperatures to be increased to mid (25-55 °C), high (55-100 °C), or very high (>100 °C) temperatures in pressurized systems and a step-wise temperature increase in the process can potentially be used to improve the performance of thickening and dewatering, which would also improve the performance of thermal processes. At higher temperatures, water molecules are more active, and it is easier to break the particle-particle and the

particle-liquid interactions (Hii et al., 2014).

The objective of this study was to investigate the impact of sludge temperature on the optimum polymer dose and conditioning of wastewater sludge and improve the performance of settling, thickening and dewatering processes by using the optimum temperature required for conditioning. The sludge temperature range selected for the study included temperatures in the range of 10 °C -100 °C that can be employed at wastewater treatment plants in non-pressurized systems.

## **4.2 Materials and Methods**

### **4.2.1 Preparation of sludge samples**

Anaerobically digested sludge samples were collected from a wastewater treatment plant in Ontario, Canada once a week. The plant digests mixed primary and secondary sludge under mesophilic temperatures. Sludge samples were stored in a refrigerator, and samples were brought to room temperature before use. A hot plate was used to increase the temperature of samples to 10 °C, 35 °C, 50 °C, 60 °C, and 100 °C in 2 L glass beakers while being stirred at 200 rpm. After reaching the target temperature, sludge samples were conditioned with a polymer as explained below.

#### **4.2.2 Preparation of polymer stock solution**

The polymer used in this study was Zetag 8160 (BASF), which is a polyacrylamide, medium-high cationic charge, a high-molecular-weight polymer that is in granular solid form. This was also the polymer that was used at the treatment plant for sludge dewatering. The polymer stock solution was prepared at a concentration of 0.5% using a jar tester (PB-700 Jartester, Phipps & Bird Inc., USA). Five g of Zetag 8160 polymer was mixed with 1 L of deionized water and stirred for first 5 min at 200 rpm followed by 55 min at 125 rpm. A hand-held blender was used to break up the remaining polymer clumps, and the polymer stock solution was left for maturation.

#### **4.2.3 Conditioning of sludge samples with polymer**

Sludge samples of 200 mL volume were spiked with polymer and mixed in 500 mL beakers using a jar tester apparatus (PB-700 Jartester, Phipps & Bird Inc., USA). Polymer doses were selected to cover the under-dose, optimum dose and over-dose polymer ranges, rapidly injected into the sludge samples, and mixed at 200 rpm for 2 min and 30 sec. After conditioning, sludge samples were used for the settling, filtration, capillary suction time (CST) and zeta potential tests as explained below. All experiments were run in triplicate, and the average values are shown in the figures. Polymer doses are reported as g/kg DS (dry solids).

#### **4.2.4 Evaluation of thickening and dewatering performance**

##### ***4.2.4.1 Capillary suction time (CST) test***

Capillary suction time (CST) test was used to evaluate the dewaterability of sludge samples after conditioning with the polymer. CST test measures the time it takes for filtered water to travel between two sensors, and shorter CST times indicate better filtration properties. A CST tester (Type 319 Multi-CST, Triton Electronics Ltd., England) was used with the CST paper (No. 17 chromatography grade paper cut into 7- × 9- cm, Whatman PLC), and the protocol outlined in the Standard Methods (APHA, 2005) was followed.

##### ***4.2.4.2 Filtration test***

Conditioned sludge samples of 200 mL were filtered for 3 minutes using 55 mm-diameter coarse filters (Fisher Scientific Ltd.) and a vacuum pump. Filtrate volume and total solids concentration of the cake remaining on the filter were measured after filtration. The total solids concentration of the cake was determined following the protocol in the Standard Methods (APHA, 2005).

##### ***4.2.4.3 Zeta potential test***

After the filtration tests, 10 mL of the filtrate from each sample was used for measuring the zeta potential. The filtrate samples were diluted by 10 times, and 10 particles were tracked to get the average zeta potential measurement for each sample. Zeta potential

measurements were performed using a zeta meter (Zeta-Meter System 4.0, GENEQ Inc.) operated at the default cell parameters of 200 V and 25 °C. Samples that were conditioned and dewatered at higher temperatures were cooled down to 25 °C before the zeta potential measurements.

#### ***4.2.4.4 Settling test***

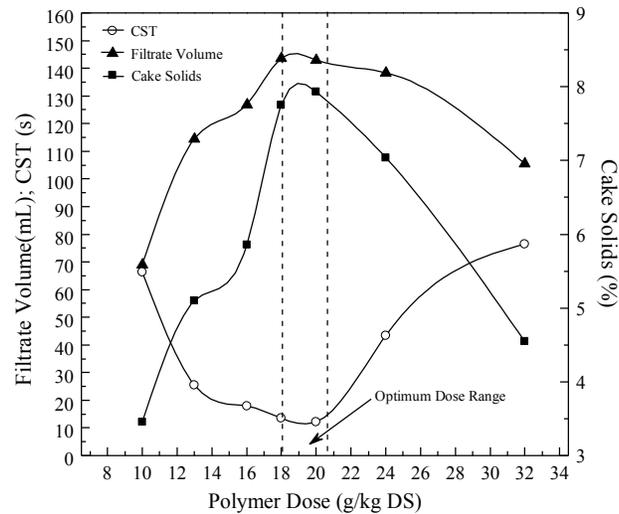
Settling tests were carried out in 100 mL graduated cylinders in triplicate. 100 mL of the conditioned sludge sample was transferred to each graduated cylinder, and the height of the interface between the solid and the liquid phases was recorded for 30 minutes. The final height of the interface indicates the settling and thickening performance of the conditioned sludge. After the settling curves were established, the slopes of the lines before the inflection point (first 60 seconds) were used to calculate the settling velocities.

## **4.3 Results and Discussion**

### **4.3.1 Sludge conditioning at 10 °C**

Fig. 4-1 illustrates the results from the CST and filtration tests after conditioning sludge at 10 °C by adding the Zetag 8160 polymer. In the under-dose range, filtrate volume and cake solids concentration increased gradually as the polymer dose approached the optimum dose. At the same time, a decrease in CST was observed which indicated water was rapidly released from conditioned sludge. At or around the optimum dose, the filtrate volume and cake solids reached their maximum values and CST reached its minimum

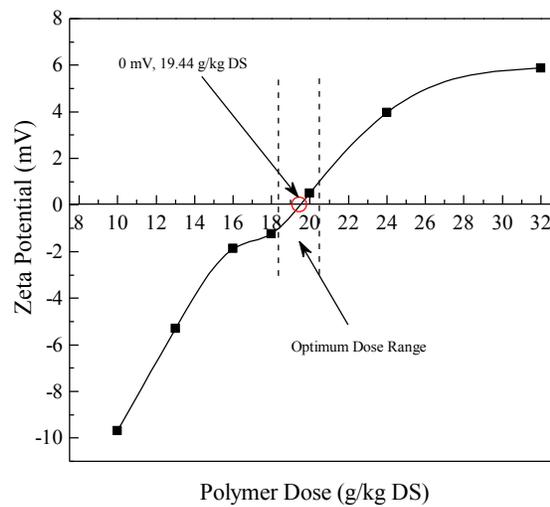
value. In the over-dose range, deterioration in filterability was observed indicated by an increase in CST and decreases in filtrate volume and cake solids. Based on the results illustrated in Fig. 4-1, optimum polymer dose at 10 °C was determined to be  $19.5 \pm 0.7$  g/kg DS (dry solids) with a CST of  $20.0 \pm 0.6$  s, filtrate volume of  $143 \pm 5$  mL, and cake solids of  $7.7 \pm 0.3$  %.



**Fig. 4-1** CST, filtrate volume and cake solids at 10 °C in the under-dose, optimum dose, and over dose ranges.

The results from the zeta potential measurements are shown in Fig. 4-2. Zeta potential is the electric potential of the particle and the surrounding double layer at the slipping plane and indicates the magnitude of the attraction-repulsion forces between particles. A strong negative or positive charge would indicate the stability of the particles in the solution, and at or around the optimum polymer dose zeta potential approaches zero (Dentel and Abu-Orf, 1993; López-Maldonado et al., 2014). Sludge particles are negatively charged and therefore zeta potential values are negative in the under-dose range. Increasing the

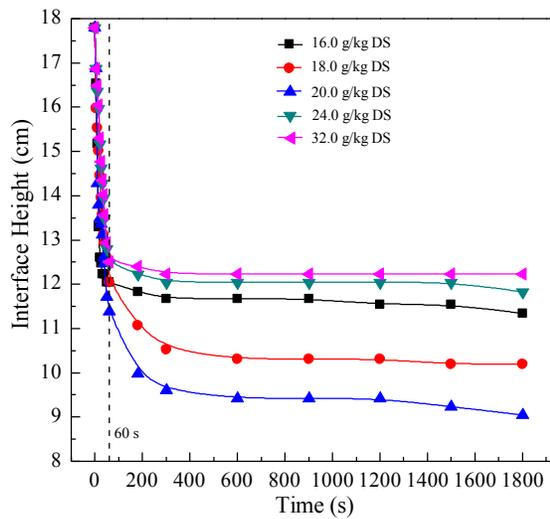
cationic polymer dose gradually decreases the magnitude of the negative zeta potential, and the zeta potential reaches a value of zero at the optimum dose. When the optimum dose is exceeded, zeta potential values obtain a positive charge that increase in magnitude with continuing polymer addition. The zeta potential measurements illustrated in Figure 4-2 point to an optimum dose of 19.44 g/kg DS, which is in accord with the optimum dose determined with the CST and filtration tests.



**Fig. 4-2** Zeta potential measurements at 10 °C at increasing polymer doses.

Settling test results showing the settling behaviour and the final interface height of the samples are presented in Fig. 4-3 and Table 4-1. The initial height of the solids-liquid interface was 17.8 cm for all samples. All samples settled rapidly in the first minute; however, the sample that was conditioned at 20 g/kg DS had the highest settling velocity (6.5 cm/min) compared to the samples that were conditioned at lower or higher polymer doses. Differences in the settling height of the interfaces were clearly seen in the first 5

minutes. The height of the final interface was lowest (9.1 cm) for the sludge sample conditioned at 20 g/kg DS indicating the best settling and compaction of solids among the doses tested. At polymer doses lower or higher than 20 g/kg DS, the height of the final interface gradually increased and was 11.8 cm at 24 g/kg DS and 10.2 cm at 18 g/kg DS. These results indicated that 20 g/kg DS was the optimum polymer dose among the doses tested.



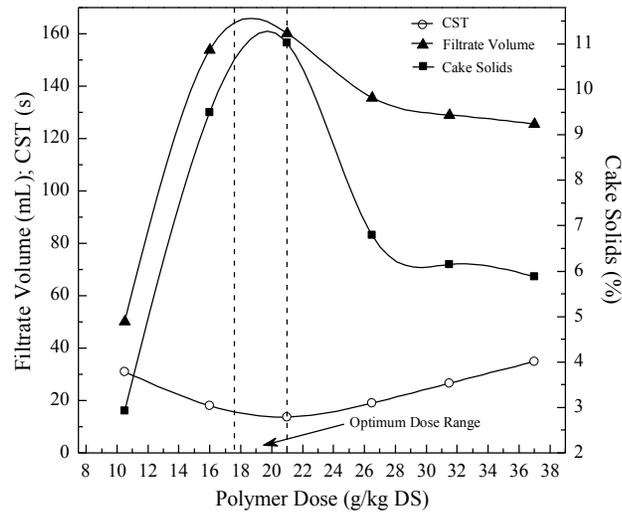
**Fig. 4-3** Settling test results at 10 °C after 30 minutes of settling.

**Table 4-1** Final interface heights (30 minutes) and average settling velocities (60 s) at 10 °C.

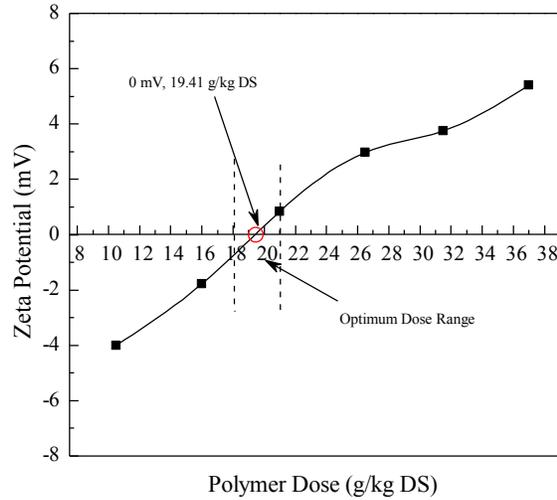
Polymer dose (g/kg DS)	Final interface height (cm)	Settling velocity (cm/min)
16.0	11.3	5.8
18.0	10.2	5.8
20.0	9.1	6.5
24.0	11.8	5.2
32.0	11.9	5.3

### 4.3.2 Sludge conditioning at 35 °C

Sludge conditioning experiments were repeated at 35 °C using the same polymer. Based on the results of the filtration and CST tests, the optimum polymer dose range emerged as  $19.3 \pm 1.4$  g/kg DS (Fig. 4-4), which resulted in  $13.9 \pm 0.4$  s of CST, 161  $\pm$  2 mL of filtrate volume and 11.0  $\pm$  0.3 % of cake solids. The zeta potential values of the particles in the filtrate samples are shown in Fig. 4-5. The polymer dose where the zeta potential reached a neutral value was around 19.41 g/kg DS, which confirms the optimum dose range determined with the filtration and CST tests (Fig. 4-4).

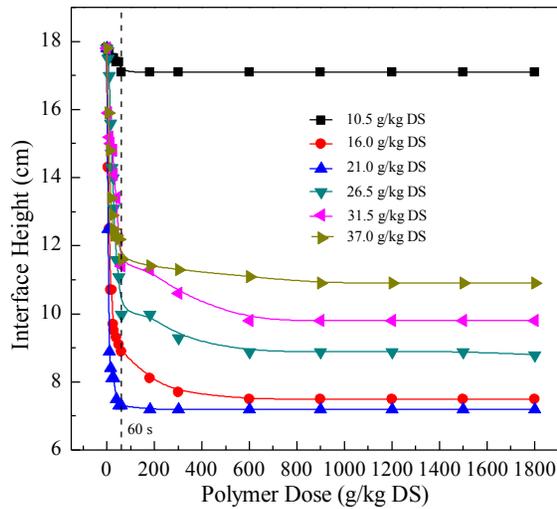


**Fig. 4-4** CST, filtrate volume and cake solids at 35 °C in the under-dose, optimum dose, and over dose ranges.



**Fig. 4-5** Zeta potential measurements at 35 °C at increasing polymer doses.

Fig. 4-6 illustrates the settling test results from sludge samples conditioned at 35 °C. Increasing the polymer dose improved the settling characteristics of sludge, and the lowest interface height (7.2 cm) after 30 min. of settling was observed at the polymer dose of 21 g/kg DS, which is in agreement with results shown in Fig. 4-4 and 4-5. The adjacent lower and higher polymer doses were 16 g/kg DS and 26.5 g/kg DS, and the interface height corresponded to 7.5 cm and 8.8 cm at these doses.



**Fig. 4-6** Settling test results at 35 °C after 30 minutes of settling.

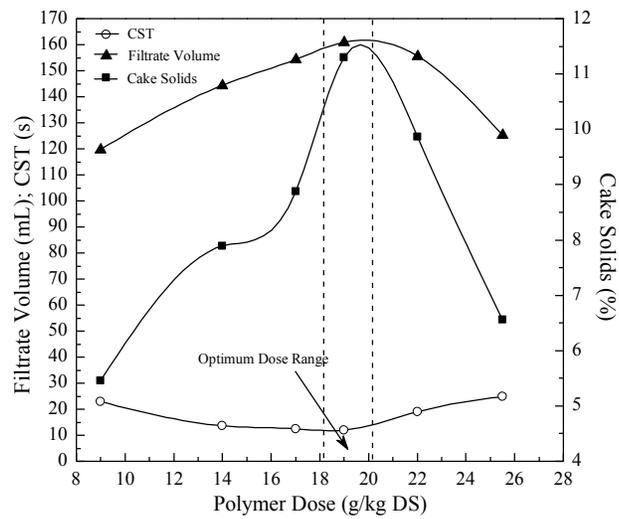
**Table 4-2** Final interface heights (30 minutes) and average settling velocities (60 s) at 35 °C.

Polymer dose (g/kg DS)	Final interface height (cm)	Settling velocity (cm/min)
10.5	17.1	0.7
16.0	7.5	8.9
21.0	7.2	10.5
26.5	8.8	7.8
31.5	9.8	6.4
37.0	10.9	6.2

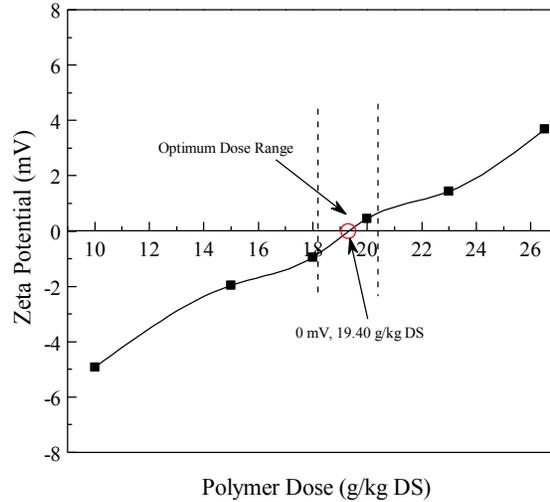
Table 4-2 illustrates the calculated average settling velocities as well as the final interface heights recorded at each dose. The fastest settling (10.5 cm/min) occurred at 21 g/kg DS, which was the optimum dose. When the polymer dose was lower or higher than 21 g/kg DS, settling velocities decreased proportionally to the increase or decrease in the polymer dose.

### 4.3.3 Sludge conditioning at 50 °C

Fig. 4-7 illustrates the results from the filtration and CST tests after conditioning sludge at 50 °C. The lowest CST ( $11.8 \pm 0.6$  s) and the highest filtrate volume ( $165 \pm 3$  mL) and cake solids ( $11.5 \pm 0.4$  %) were measured at  $19.2 \pm 0.9$  g/kg DS. Zeta potential measurements also indicated the optimum dose as 19.40 g/kg DS where a neutral value for the zeta potential was achieved (Fig. 4-8).

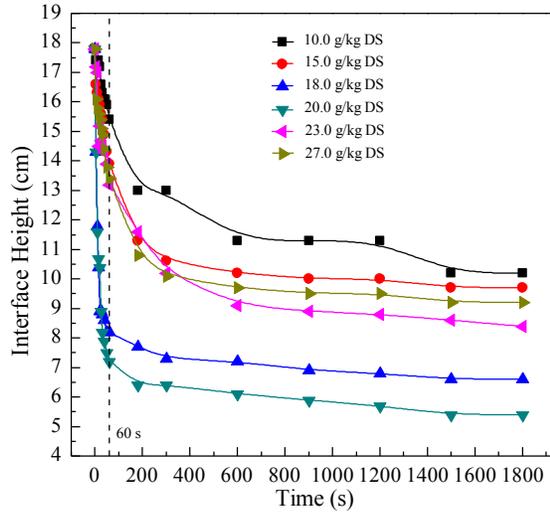


**Fig. 4-7** CST, filtrate volume and cake solids at 50 °C in the under-dose, optimum dose, and over dose ranges.



**Fig. 4-8** Zeta potential measurements at 50 °C at increasing polymer doses.

Fig. 4-9 illustrates the settling performances of conditioned sludge samples at 50 °C in the dose range of 10-27 g/kg DS. Among the doses tested, the best settling performance was observed at 20 g/kg DS, which resulted in the lowest interface height. At polymer doses lower or higher than 20 g/kg DS, settling characteristics of sludge deteriorated and resulted in a higher interface height. The calculated settling velocities and the final interface heights are reported in Table 4-3. The highest settling velocity, 12.6 cm/min, was obtained at the polymer dose of 20 g/kg DS, and this corresponded to the lowest interface height of 5.4 cm.



**Fig. 4-9** Settling test results at 50 °C after 30 minutes of settling.

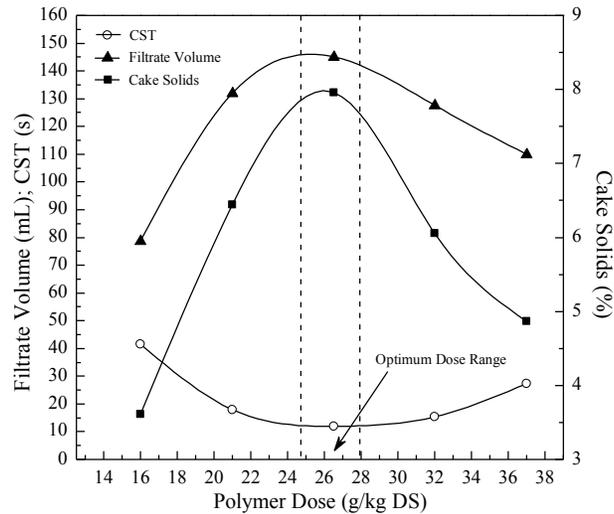
**Table 4-3** Final interface heights (30 minutes) and average settling velocities (60 s) at 50 °C.

Polymer dose (g/kg DS)	Final interface height (cm)	Settling velocity (cm/min)
10.0	10.2	2.4
15.0	9.7	3.9
18.0	6.6	9.6
20.0	5.4	12.6
23.0	8.4	4.6
27.0	9.2	4.4

#### 4.3.4 Sludge conditioning at 60 °C

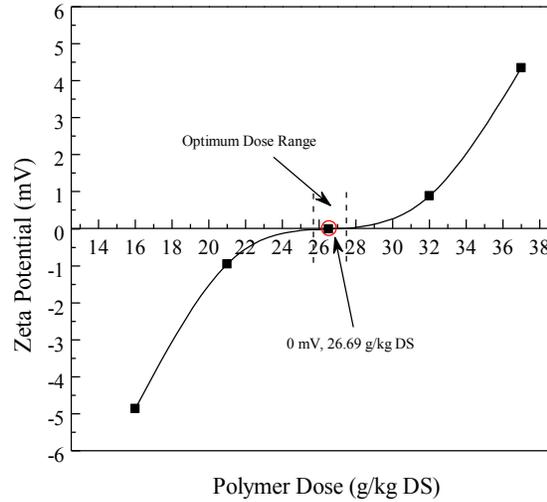
Fig. 4-10 illustrates the results of the filtration and CST tests after conditioning sludge at 60 °C. The optimum dose range was identified as  $26.5 \pm 1.5$  g/kg DS, with CST of  $12.3 \pm 0.5$  s, the filtrate volume of  $146 \pm 3$  mL and the cake solids of  $7.7 \pm 0.3$  %. These results showed a deterioration in sludge filtration compared to the results obtained at 50 °C. Heating at these higher temperatures started dissolving solids and breaking up large particles, which increased the polymer demand due to the generation of more negatively

charged surfaces.



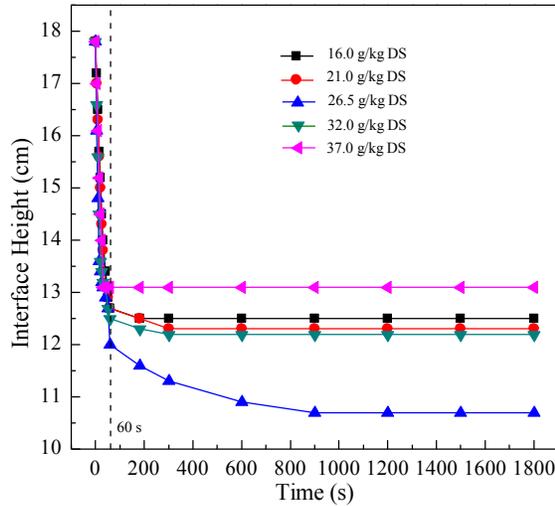
**Fig. 4-10** CST, filtrate volume and cake solids at 60 °C in the under-dose, optimum dose, and over dose ranges.

As the zeta potential results show in Fig. 4-11, a higher polymer dose (26.5 g/kg DS) was needed to neutralize the zeta potential at 60 °C. At 20 g/kg DS, which was the optimum dose for the temperatures lower than 50 °C, the zeta potential value was approximately -1.5 mV. With increasing temperatures, the binding between the polymer and sludge particles weakens, and the efficiency of flocculation decreases (Meid et al., 2012). Therefore, more polymer is needed to achieve the same level of conditioning and flocculation at higher temperatures.



**Fig. 4-11** Zeta potential measurements at 60 °C at increasing polymer doses.

Results from settling tests at 60 °C are shown in Fig. 4-12 and Table 4-4. Among the doses tested, 26.5 g/kg DS resulted in the highest settling velocity (5.8 cm/min) and the lowest interface height (10.7 cm). The presence of large quantities of bubbles was also observed during settling. Compared to other temperatures (e.g., 35 °C and 50 °C), both the settling velocity and the height of the interface got worse at 60 °C in spite of adding more polymer. The binding ability of polyacrylamide is decreased after around 60 °C (Sakohara et al., 2007) which can also explain the decreased effectiveness of the polymer and the higher polymer doses required at higher temperatures.



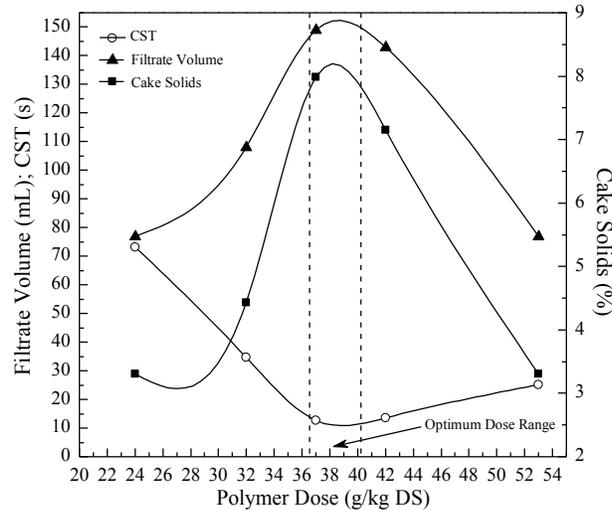
**Fig. 4-12** Settling test results at 60 °C after 30 minutes of settling.

**Table 4-4** Final interface heights (30 minutes) and average settling velocities (60 s) at 60 °C.

Polymer dose (g/kg DS)	Final interface height (cm)	Settling velocity (cm/min)
16.0	12.5	5.1
21.0	12.3	5.1
26.5	10.7	5.8
32.0	12.2	5.3
37.0	13.1	4.7

#### 4.3.5 Sludge conditioning at 100 °C

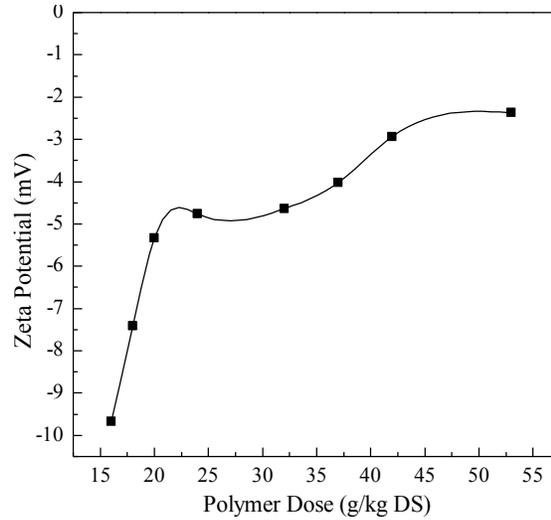
The polymer doses required for sludge conditioning at 100 °C were drastically higher (Fig. 4-13). The optimum dose at this temperature was  $38.5 \pm 1.2$  g/kg DS, which was almost double the dose at 50 °C. In the optimum dose range, CST was  $12.8 \pm 0.3$  s, filtrate volume was  $149 \pm 3$  mL, and cake solid concentration was  $7.9 \pm 0.3$  %. Increasing the sludge temperature, increased the polymer demand of the sample.



**Fig. 4-13** CST, filtrate volume and cake solids at 100 °C in the under-dose, optimum dose, and over dose ranges.

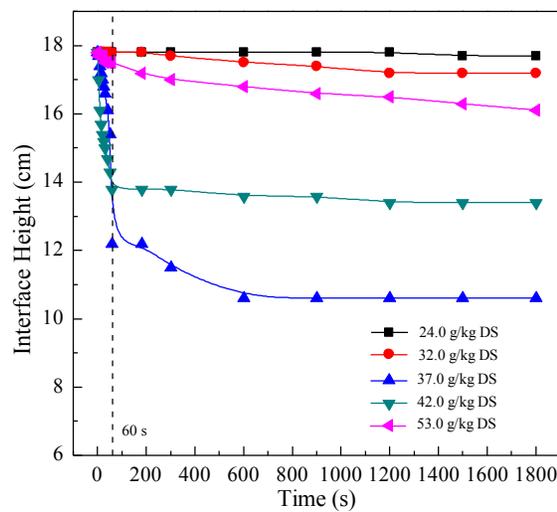
Fig. 4-14 illustrates that the zeta potential results. At the starting polymer dose of 15 g/kg DS, the zeta potential was approximately -10 mV, which was 5 times more than the zeta potential values measured around 15 g/kg DS at other temperatures tested. Increasing the polymer dose decreased the magnitude of the zeta potential, but even at the highest polymer dose of 55 g/kg DS, charge neutralization was not achieved. The filtration based tests indicated an optimum dose of 38.5 g/kg DS, but the zeta potential at this dose was still -4 mV. This can be explained by the different temperatures that the measurements were carried at. The CST and filtration tests were conducted with sludge at 100 °C but the zeta potential measurements had to be done at 25 °C due to the constraint of the zeta-meter. The solubility of acrylamide sharply increases after 50 °C (Uğuzdoğan et al., 2013), and therefore when the temperature of filtrate is decreased from 100 °C to 25 °C, zeta potential measurements will underestimate the quantity and effectiveness of the

dissolved polymer in the solution. This would explain the negative zeta potential of -4 mV at the optimum dose of 38.5 g/kg DS at 100 °C.



**Fig. 4-14** Zeta potential measurements at 100 °C at increasing polymer doses.

The settling test results at 100 °C are illustrated in Fig. 4-15 and Table 4-5. The lowest height of the interface (7.9 cm) and the highest settling velocity (4 cm/min) was observed at 37 g/kg DS, which was also the optimum dose determined by the filtration tests.



**Fig. 4-15** Settling test results at 100 °C after 30 minutes of settling.

**Table 4-5** Final interface heights (30 minutes) and average settling velocities (60 s) at 100 °C.

Polymer dose (g/kg DS)	Final interface height (cm)	Settling velocity (cm/min)
24.0	17.7	0.1
32.0	17.2	0.1
37.0	7.9	4.0
42.0	13.4	3.8
53.0	16.1	0.3

#### 4.3.6 Comparison of conditioning performance at different temperatures

**Table 4-6** Summary of results at each temperature

T (°C)	Optimum Dose (g/kg DS)	CST (s)	Filtrate Volume (mL)	Cake Solids (%)	Settling Velocity (cm/min)
10	19.5 ± 0.7	20.0 ± 0.6	143 ± 5	7.7 ± 0.3	6.5
35	19.3 ± 1.4	13.9 ± 0.4	161 ± 2	11.0 ± 0.3	10.5
50	19.2 ± 0.9	11.8 ± 0.6	165 ± 3	11.5 ± 0.4	12.6
60	26.5 ± 1.5	12.3 ± 0.5	146 ± 3	7.7 ± 0.3	5.8
100	38.5 ± 1.2	12.8 ± 0.3	149 ± 3	7.9 ± 0.3	4.0

Table 4-6 presents the optimum dose, CST, filtrate volume, cake solids, and settling velocity obtained at each temperature tested (10 °C, 35 °C, 50 °C, 60 °C and 100 °C) to provide a comparison of results. The optimum dose required to condition the sludge was very similar (19.2-19.5 g/kg DS) at 10, 35, and 50 °C; however, the ability of sludge to release its water was significantly different. Increasing the temperature until 50 °C improved the thickening and filtration characteristics of conditioned sludge, and the highest filtrate volume (165 mL), cake solids (11.5%) and settling velocity (12.6 cm/min) were observed at 50 °C. Increasing the sludge temperature further to 60 °C and 100 °C not only increased the polymer demand substantially but also decreased the ability of

sludge to release its water. The optimum polymer dose was 26.5 g/kg DS at 50 °C , and 38.5 g/kg DS at 100 °C. At 100 °C, the filtrate volume was reduced to 149 mL, and the settling velocity was only 4 cm/min.

#### **4.4 Conclusions**

In this study, the temperature was found to be an important factor that impacts sludge conditioning, optimum polymer dose, and thickening and dewatering performance. A wide range of sludge temperatures (10 °C, 35 °C, 50 °C, 60 °C and 100 °C) were tested. In the temperature range of 10 °C to 50 °C, the polymer dose required for conditioning was similar but resulted in different thickening and dewatering performance. The best results were observed at 50 °C, where the highest filtrate volume, cake solids, and settling velocity were obtained at a polymer dose of 19.2 g/kg DS. Thickening and dewatering performance was also very good at 35 °C. Increasing the sludge temperature further to 60 °C and 100 °C increased the polymer demand up to 38.5 g/kg DS and deteriorated the thickening and dewatering performance. The results of this research show that sludge conditioning at 35-50 °C can significantly improve treatment performance and result in savings for treatment plants. There would be no additional cost for heating sludge at wastewater treatment plants where thermal treatment processes (e.g., thermal hydrolysis, wet oxidation, super critical water oxidation) are used, and a step-wise temperature increase before thickening or dewatering can be easily incorporated in the treatment train.

## **Acknowledgment**

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## **CHAPTER 5**

### **5 Supercritical Water Oxidation for Treatment of Wastewater Sludge and p-tert-butylcatechol (TBC)**

#### **Abstract**

This study investigated the performance of the SCWO treatment for wastewater sludge and the degradation of p-tert-butylcatechol (TBC) under a range of operational conditions including sludge solids content (2-12 %), TBC concentration (0.1-1 %), reactor temperature (400-550 °C), reactor pressure (18-28 MPa), oxygen excess (n=1-8) and residence time (1-30 minutes). Treatment performance was evaluated by measuring the chemical oxygen demand (COD) and using Fourier Transform Infrared Spectroscopy (FTIR). The best operational conditions for sludge treatment were found to be T=550 °C, P=25 MPa, n=5, and t=10 minutes. SCWO was shown to be very effective for sludge treatment, and over 99% COD removal could be achieved under these conditions. The addition of TBC decreased the percent COD removal but still 98% COD removal with final COD values less than 50 mg/L could be achieved. Sludge treated with SCWO can be safely discharged to the environment without causing any concerns for public health or the environment.

#### **Keywords**

Supercritical water oxidation (SCWO), wastewater, sludge, p-tert-butylcatechol (TBC), treatment

## 5.1 INTRODUCTION

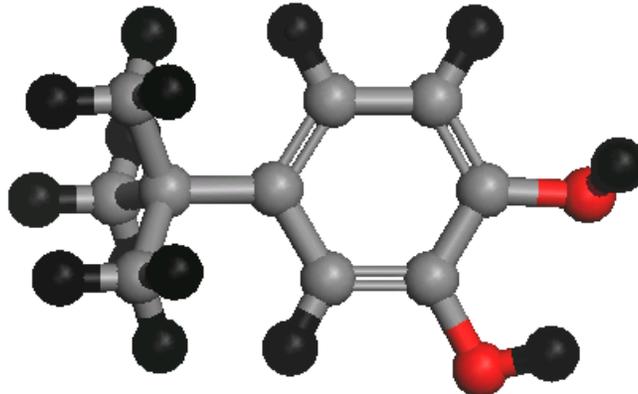
Sewage sludge treatment consumes approximately half of the capital cost and more than half of the operational cost of a wastewater treatment plant (WWTP) (Novak, 2006). Various approaches to sludge management and disposal include land application (Bondarczuk et al., 2016), landfilling (Zhu and Zhao, 2010), incineration (Han et al, 2015), and in recent years supercritical water oxidation (SCWO) is being considered due to the advancements made in the SCWO technology (Xu et al, 2012). Municipal sludge contains organic matter as well as pathogens, heavy metals, toxic chemicals, and other emerging contaminants. SCWO is an efficient and environmentally benign method that can achieve complete degradation of organic compounds, stabilization of heavy metals, elimination of odours, and destruction of pathogens (Zhang et al., 2016). In addition, SCWO produces reusable end products such as clean water, carbon dioxide, minerals, and metals. Heat generation is a by-product of the process, which can be utilized on-site or used for energy production.

Supercritical water is a state of water achieved when the pressure and temperature are higher than the thermodynamic critical point of water (374 °C and 22.1 MPa). At this state, liquid and vapour co-exist, water becomes an excellent non-polar solvent for both organic molecules and oxidants (e.g. O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, etc.). SCWO technology takes advantage of unique physical and chemical properties of supercritical water such as high diffusivity, low viscosity, zero surface tension, controllable dielectric constant, reduced effect of

hydrogen bonds, and excellent miscibility with organic wastes and oxygen (Zhang et al., 2016). Complex organic compounds dissolve into simple molecules and decompose to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the presence of an oxidant that is added during the process. Even long carbon chains and aromatic rings can be rapidly degraded when both the water temperature and pressure are higher than the critical point (Qian et al., 2016). In supercritical water, the organic compounds and the oxidants can be dissolved in a single-phase, resulting in a higher reactivity due to the high frequency of the molecular collision between the oxidants and the organic compounds (Veriansyah and Kim, 2007). If hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is chosen as the oxidant, which is commonly used in SCWO applications due to its low-cost and ease of use,  $\text{H}_2\text{O}_2$  is rapidly converted to hydroxyl radicals ( $\bullet\text{OH}$ ) in the supercritical state of water, and promote the decomposition reaction of the organic compounds (Robert et al, 2002).

Considering the above-mentioned advantages, SCWO is a promising clean/green technology for the treatment of sludge containing various recalcitrant pollutants. SCWO method showed high efficiency in the treatment of both sewage and industrial sludge containing recalcitrant organic and inorganic compounds (Williams and Onwudili, 2006). Several studies demonstrated the potential of SCWO for the treatment of sewage sludge at pilot-scale (Xu et al., 2012). The CEAB Corp. (Chematur Engineering AB, Sweden) built the first pilot-scale plant in Europe for the sewage sludge treatment with a design flow of  $7 \text{ m}^3/\text{h}$  (Gidner and Stenmark, 2001). Since then several pilot-scale facilities were

constructed and operated in Europe, North America, China and Russia for the treatment of domestic and industrial sludge as well as hazardous industrial waste (Zhang et al., 2016). Xu et al. (2012) designed an SCWO pilot plant specifically for sewage sludge treatment in China, and the authors showed the commercial feasibility of the SCWO for sludge treatment, management, and disposal. Harlingen Wastewater Treatment Plant (Harlingen, Texas, US) ran a pilot-scale SCWO facility for sludge treatment, which also validated the feasibility and applicability of the SCWO for municipal applications (Griffith and Raymond, 2002). There is now a full-scale and operational SCWO facility in China, which is used as the only method of sludge treatment at a large wastewater treatment plant in Tianjin.



**Fig. 5-1** Molecular model of *p*-tert-butylcatechol (TBC)

(Source: <http://dx.doi.org/10.1080/00986445.2016.1262359>)

*p*-tert-butylcatechol (TBC) is a recalcitrant aromatic organic compound that is very resistant to biological treatment. TBC is widely used in the industry and may be present

at high concentrations in wastewater and sludge. TBC molecule (Fig. 5-1), has three substituents on position 1, 2 and 4 of the aromatic ring, respectively with two hydroxyl groups and one butyl group. It is highly resistant to degradation due to the high density of delocalized electrons ( $\pi_8^8$ , 8 electrons on 8 centers), which increase the difficulty of molecular ring-opening mechanisms (Yan et al., 2016). Also, there is a possibility of hydrogen bond formation between the hydroxyl groups of TBC surrounded by the cluster of water molecules.

For liquid wastes, such as sludge, typically an organic content of 1-20 % is required for successful SCWO applications (Marrone, 2013). For SCWO of sludge, an initial 8-10 % solids concentration is desired (Sloan et al., 2009), which means a prior thickening process would be needed. At these solids concentrations, the temperature at which the heat release exceeds the heat input is 250 °C, and the highest desirable temperature is 600 °C, which is the temperature that all organics are converted to water and carbon dioxide within seconds. At temperatures lower than 600 °C, nitrous oxide is not formed, and this eliminates the need for gas scrubbing (Sloan et al., 2009).

The initial solids concentration of sludge is one of the factors that determines the performance and feasibility of the SCWO process. In addition, operational parameters such as temperature, pressure, oxygen excess, and residence time determine the removal efficiency of the organic compounds. This study used TBC as a model recalcitrant

organic contaminant and investigated the effect of (a) initial solids concentration on the treatment of sludge under a range of temperature, pressure and excess oxygen scenarios during SCWO operation, and (b) degradation of TBC under a range of temperature, pressure and excess oxygen scenarios during SCWO operation. The objective of the study was to determine the performance of the SCWO treatment for wastewater sludge and investigate the degradation of recalcitrant organic compounds, such as TBC, under a range of operational conditions.

## **5.2 MATERIALS AND METHODS**

### **5.2.1 Sludge samples**

The anaerobically digested sludge was obtained from the Beichen Wastewater Treatment Plant (Tianjin, China). The total solids content of the sludge sample after drying at 105 °C for 24 h was measured as 5.2 % (wt). For the SCWO experiments, sludge samples with solids concentrations of 2, 4, 6, 8, 10, and 12 % (wt) were prepared by first drying the sludge in the oven and then adding deionized water (DI).

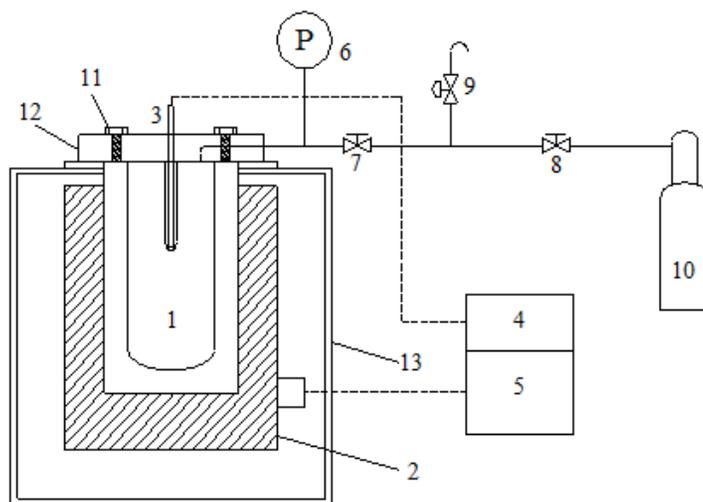
### **5.2.2 Reagents**

Hydrogen peroxide 30 % (w/w) (Jiangtian Industry Co., Ltd, Tianjin, China) was used as the oxidant for the SCWO process. The stock solution of the TBC was prepared by dissolving the chemical in the DI water to give a final concentration of 0.15 % (wt). TBC was then spiked in sludge samples to give the desired concentrations of 0.1, 0.5, and 1 %

(wt) before the SCWO treatment.

### 5.2.3 SCWO Reactor

A high-pressure and high-temperature reaction vessel (Runchang Petrochemical Equipment Co., Ltd, Dalian, China) was used in this study for the SCWO reaction (Fig. 5-2). The volume of the reactor is 0.5 L, the design maximum temperature is 650 °C, and the design maximum pressure is 30 MPa. The working temperature and pressure are recommended not to exceed 600 °C and 25 MPa, respectively. The total power of the heater is 2.5 kW. During the operation of the SCWO, 0.5 L sample volumes of sludge were used with different solids and TBC concentrations.



**Fig. 5-2** SCWO set-up– 1: Reaction Vessel; 2: Heater; 3: Thermal couple; 4: Thermal meter; 5: Thermal meter for the heater; 6: Pressure sensor and pressure indicator; 7, 8: Gate valves; 9: Air release valve (globe valve); 10: Nitrogen cylinder; 11: Screws; 12: Vessel cap; 13: Vessel bracket

## **5.2.4 Determination of treatment performance**

### ***5.2.4.1 Chemical Oxygen Demand (COD)***

Chemical Oxygen Demand (COD) test kits by HACH were used for measuring the initial and remaining (residual) COD in sludge, and the percent COD removal after SCWO treatment. The COD test is achieved via two steps that include sample digestion and measurement. Digital Reactor Block (DRB) 200 was used for the digestion of the sludge samples. For COD analysis, 2 mL of the aqueous sludge sample was mixed with the COD reagents and digested at 150 °C and incubated for 2 h. A blank sample was prepared using 2 mL DI water and following the same procedure for the COD test. After cooling down the test tube contents, the tubes were placed into the HACH spectrophotometer cell, and the COD values were measured.

### ***5.2.4.2 Fourier Transform Infrared Spectroscopy (FTIR)***

The degradation level of organic compounds in sludge samples before and after the SCWO treatment was measured using Fourier Transform Infrared Spectroscopy (FTIR) (NICOLET iS10, Thermo Scientific, US). FTIR provides an infrared spectrum of absorption or emission, and it is particularly effective on polymers and organic compounds. When a sample is exposed to infrared radiation (IR), some of the radiation is absorbed by interatomic bonds at varying intensities and at varying frequencies resulting the bonds to vibrate in different motions such as stretching and bending. The resulting spectrum represents a fingerprint of the sample, and the peaks can be directly correlated

to the bonds within the compound. The quantity of the OH groups, C-C and C=C bonds can be determined based on the stretching and vibration of these bonds. The stretching and vibration of the interatomic bonds change due to the splitting of the bonds in the carbon chains and the aromatic rings after the SCWO treatment. Therefore, the differences in the FTIR spectra before and after SCWO can be utilized to evaluate the extent of degradation of the organic compounds in sludge samples. The FTIR spectra were recorded using a Bruker Vertex 70 FTIR Spectrometer in the IR spectrum of 700~4500  $\text{cm}^{-1}$  with the resolution of 4  $\text{cm}^{-1}$ .

## **5.3 RESULTS AND DISCUSSION**

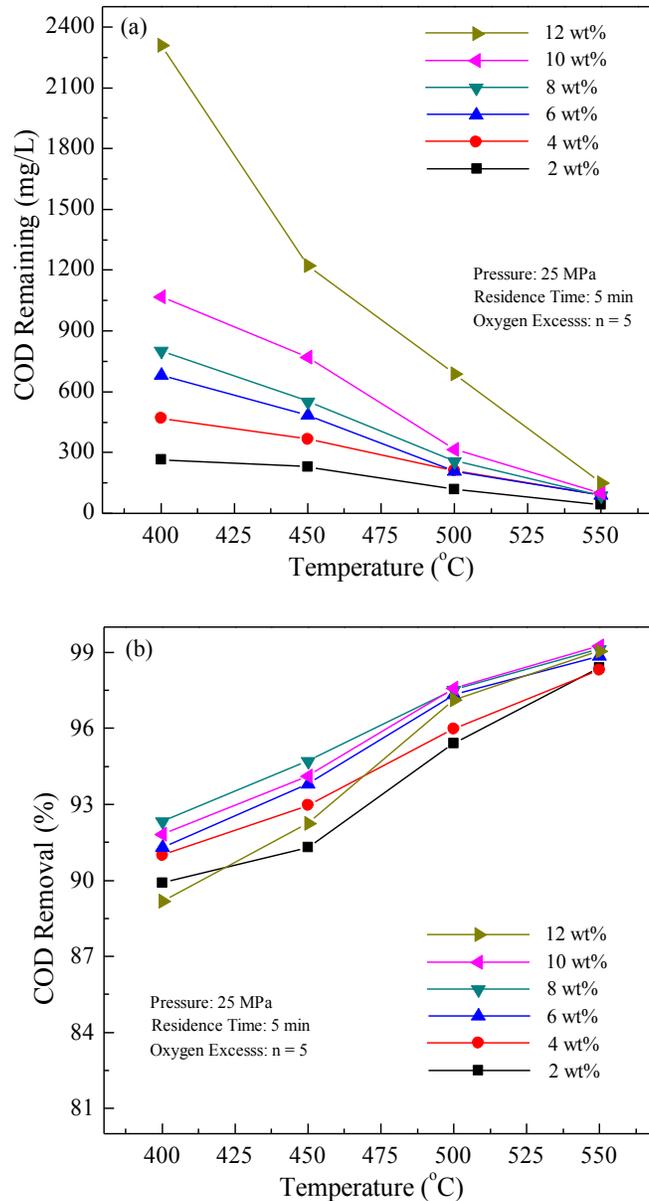
### **5.3.1 Solids content of samples for SCWO treatment**

The initial solids content of sludge is expected to play significant a role in determining the SCWO treatment performance and efficiency. Water is needed for the SCWO reaction, and not having enough water may decrease the efficiency of the process. Sludge samples with initial solids concentrations of 2, 4, 6, 8, 10, and 12 % were prepared and treated in the SCWO reactor under a range of reactor temperature and pressure conditions and excess oxygen contents. The initial COD of the untreated 2, 4, 6, 8, 10, and 12 % sludge samples were 2620, 5230, 7850, 10500, 13100, and 15800 mg/L, respectively.

#### ***5.3.1.1 Effect of temperature***

To investigate the effect of temperature, the reactor temperature was varied (400 °C, 450 °C, 500 °C and 550 °C) while all other operational parameters were kept constant. Sludge

samples with solids contents of 2 %, 4 %, 6 %, 8 %, 10 % and 12 % were prepared and treated at each of the above temperatures under a pressure of 25 MPa, oxygen excess of n = 5, and the residence time of 10 min.



**Fig. 5-3** Optimization of initial sludge solids content and the effect of temperature: (a) COD remaining; (b) COD removal

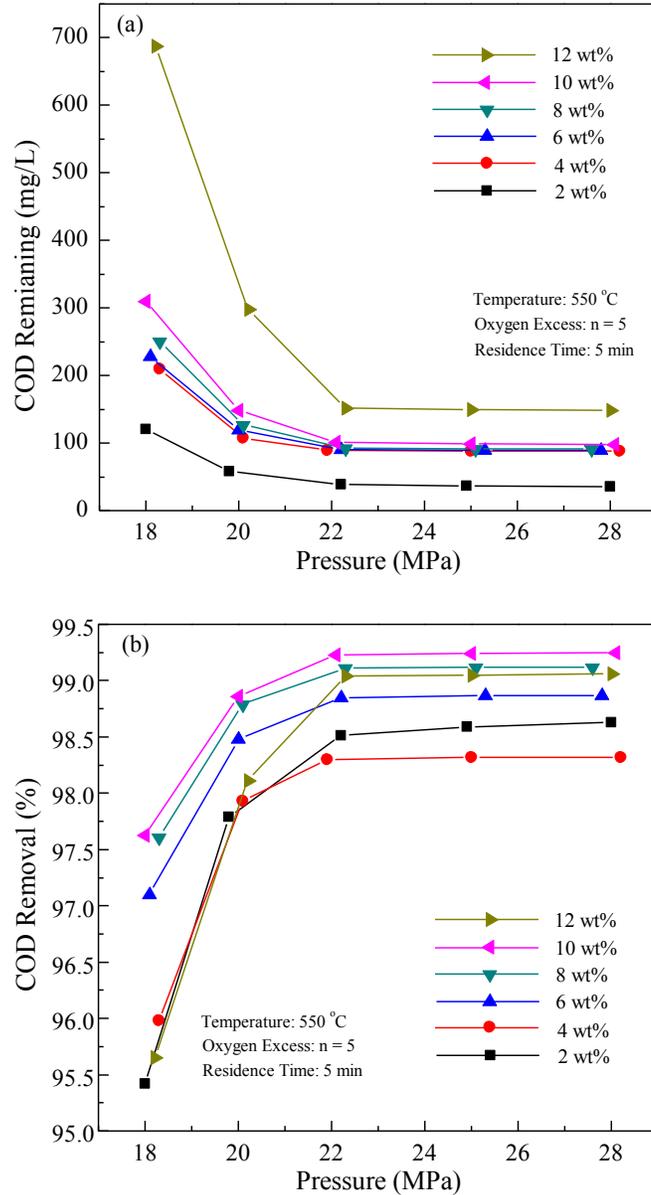
Fig. 5-3 (a) shows the residual COD remaining in sludge samples after SCWO treatment at different temperatures. Increasing the SCWO temperature decreased the remaining COD in sludge samples. Samples with higher solids content had substantially higher COD values after treatment at 400 °C, but the COD difference among the samples gradually decreased until 550 °C was reached. For example, the COD contents of the 2 % and 12 % samples were 265 and 1710 mg/L at 400 °C, and only 42 and 149 mg/L at 550 °C, respectively.

Fig. 5-3 (b) illustrates the percent COD removal of the sludge samples at different temperatures. Overall, excellent percent COD removals were achieved ranging between 89-99 % for all samples. Increasing the SCWO temperature increased the percent COD removal, and all samples had higher than 95 % COD removal at 500 °C. Highest percent COD removals were observed at 550 °C. Increasing the solids content increased the percent COD removal until 8 % solids content was reached, but beyond that increasing the solids content decreased the percent COD removal. Thus, the sample with the solids content of 8 % had the highest percent COD removal at all temperatures compared to all other samples.

### ***5.3.1.2 Effect of pressure***

In order to evaluate the effect of pressure, the reactor pressure was varied between 18 and 28 MPa in increments of 3 MPa. The sludge samples of 2, 4, 6, 8, 10 and 12 % solids

content were treated at these pressure values while the reactor temperature was kept at 500 °C, oxygen excess of  $n = 5$ , and the residence time of 10 min.



**Fig. 5-4** Optimization of initial sludge solid content and the effects of pressure: (a) COD remaining; (b) COD removal

Fig. 5-4 (a) illustrates the residual COD trends for sludge samples under different reactor

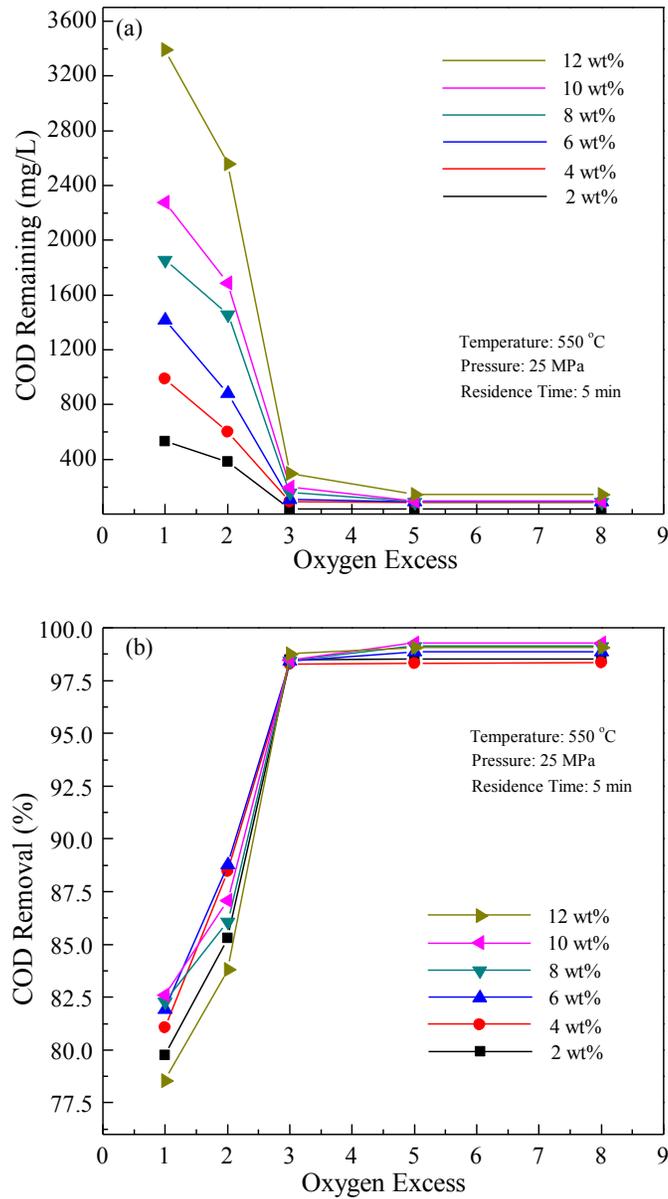
pressures. A rapid decrease in COD was observed until 22 MPa was reached, but higher reactor pressures (25 and 28 MPa) did not have any significant effect on COD. 22 MPa is the critical point pressure of water, and at or over the critical point, the distance among the water molecules decrease, which can cause the formation of clusters of water molecules (Zhao et al., 2015). The higher numbers of water clusters can hinder the collisions between the water molecules and the oxidants. This can explain why higher pressures do not further improve the COD removal.

Fig. 5-4 (b) illustrates the percent COD removal in the same samples. Increasing the solids concentration until 10 % increased the percent COD removal, but a substantial decrease in COD removal was observed when the solids concentration was increased to 12 %. At a pressure of 18 MPa, the percent COD removal for the 10 % sample was 97.6 %, whereas the percent COD removal for the 12 % sample was 95.6 %. The percent COD removal of the 8 % sample closely followed the 10 % sample, and the difference between the COD removals was approximately 0.1 %.

### ***5.3.1.3 Effect of oxygen excess***

Excess oxygen is another important operational parameter for the SCWO process. Excess oxygen is defined as the ratio between the added oxidant and the COD of the sample. If the molar amount of oxidant is five times the COD of the sample, the oxygen excess is  $n = 5$ . For SCWO reactions,  $n$  must have a minimum value of 1. Lower  $n$  values would

result in supercritical water gasification ( $n=0$ ) or supercritical water partial oxidation ( $0 < n < 1$ ) (Qian et al., 2016). In these experiments,  $n$  values of 2, 3, 5 and 8 were tested, and sludge samples with 2, 4, 6, 8, 10 and 12 % solids content were tested at a constant temperature of 500 °C, the pressure of 25 MPa, and the residence time of 10 min.



**Fig. 5-5** Optimization of initial sludge solid content and the effects of oxygen excess: (a) COD remaining; (b) COD removal

As shown in Fig. 5-5 (a) and (b), increasing the oxygen access increases the degradation and percent removal of COD. Rapid improvements are observed at n=1, 2, and 3, but beyond 3 there is little change in the COD values since almost complete oxidation is achieved. However, for the 12 % solids sample that had a higher initial COD value, a significant reduction in COD (from 198 to 146 mg/L) was observed at n=5. Percent COD removal of the 12 % sample was again lower than the other samples, and the 8 % and 10 % solids samples had some of the highest COD removals.

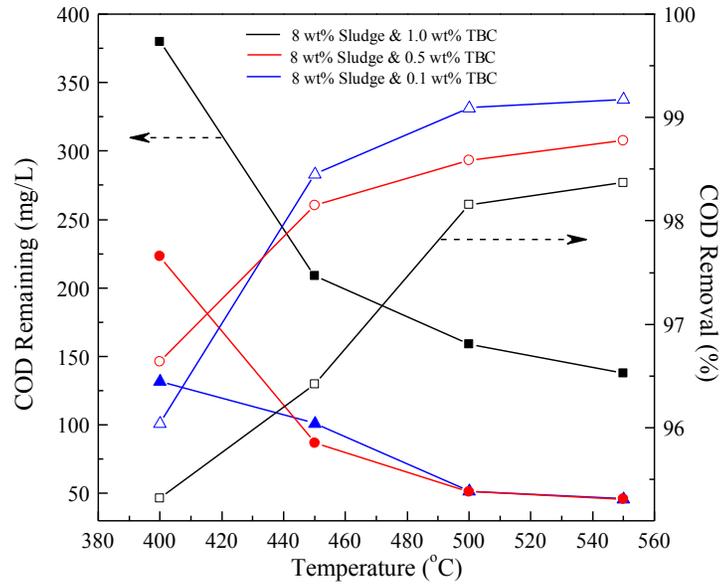
Based on the knowledge obtained from the above experiments, it appeared that both 8 % and 10 % solids concentration in sludge would work equally well for the SCWO. Wastewater sludge typically has a solids concentration of 3-6 % after biological treatment and is thickened before sludge treatment. It is easier and cheaper to achieve 8 % solids content compared to 10 %, and mechanical thickeners would be required to achieve 10 % solids, whereas 8 % solids concentration can be achieved with gravity thickeners. For this reason, 8 % solids concentration was chosen to be used in the remainder of the experiments where the degradation of TBC with the SCWO was studied.

### **5.3.2 Degradation of TBC with SCWO**

In the next phase of the experiments, three different concentrations of TBC (0.1, 0.5 and 1.0 % (wt)) were added to sludge that had a solids content of 8 %. The initial COD values of these samples were 3351 mg/L, 6443 mg/L, and 8115 mg/L, respectively. TBC was

chosen as a model recalcitrant organic contaminant in these experiments. The operation parameters were optimized, and the FTIR spectroscopy was used for the evaluation of degradation of TBC and sludge constituents after the SCWO treatment.

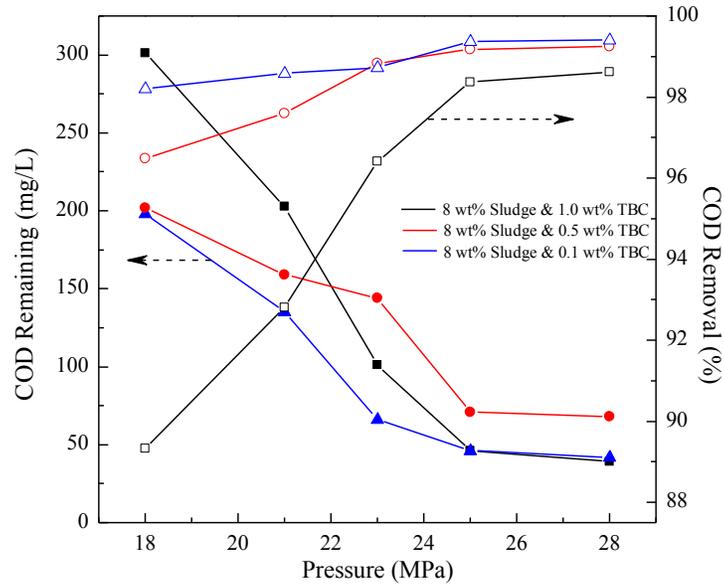
### 5.3.2.1 Effect of temperature



**Fig. 5-6** Effect of temperature on SCWO treatment of sludge spiked with TBC

Fig. 5-6 illustrates the effect of temperature on the SCWO treatment of 8 % sludge that was spiked with TBC. The pressure, residence time and oxygen excess used were 25 MPa, 10 min, and n=3, respectively. Reactor temperatures of 400, 450, 500 and 550 °C were tested. As shown in Fig. 5-7, the residual COD exhibited a sharp decrease until 500 °C was reached, and at 550 °C the residual COD was the lowest for all samples. The residual COD remaining in sludge was also related to the initial TBC concentrations, and

followed the order of  $COD_{1\%TBC} > COD_{0.5\%TBC} > COD_{0.1\%TBC}$ . At 550 °C, samples with 0.5% and 0.1% TBC had residual COD values lower than 50 mg/L, but the 1 % TBC sample still had approximately 150 mg/L COD.



**Fig. 5-7** Effect of pressure on SCWO treatment of sludge spiked with TBC

The percent COD removal efficiencies were inversely proportional to the initial TBC concentrations, and the higher the TBC concentration the lower the percent removal was. The highest percent COD removals were observed at 550 °C and ranged between 98.4 % (for 1 % TBC) and 99.3 % (for 0.1 % TBC). The results indicated that compared to the previous experiments (Fig. 5-3) where sludge samples had no TBC, the COD removal efficiency for sludge samples with TBC was lower. As the amount of TBC increases, more hydrogen bonds are likely to be formed, which hinders the degradation. Also, as the TBC molecule has two hydroxyl groups and one tert-butyl group, TBC addition may

increase the viscosity of sludge which lowers the probability of molecular collision between oxidants and sludge particles. The tert-butyl group in the TBC increases the steric hindrance preventing chemical reactions with the oxidant molecules. This is another reason why TBC amount can affect the COD removal of the samples during the SCWO processes.

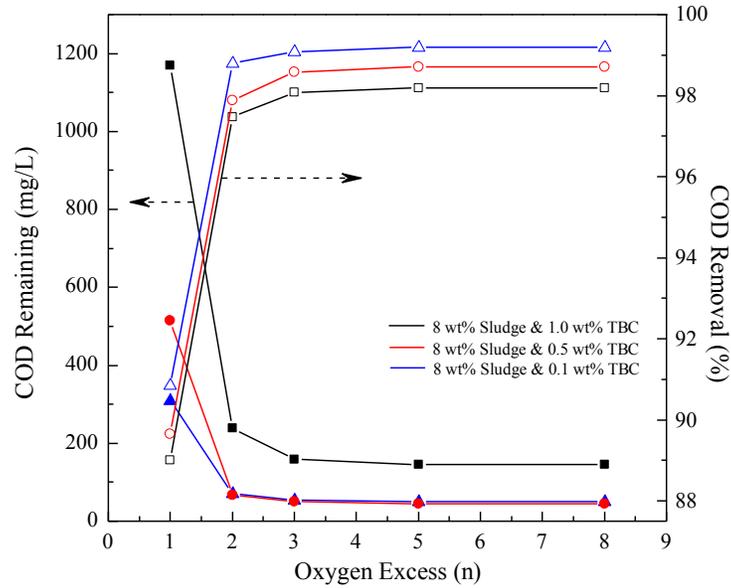
### ***5.3.2.2 Effect of pressure***

Fig. 5-7 shows the effect of pressure on the SCWO treatment of 8 % sludge that was spiked with different concentrations of TBC. The temperature, residence time and oxygen excess were kept at 550 °C, 10 min, and  $n=5$ , respectively. Pressure values of 18, 21, 23, 25 and 28 MPa were tested. As shown in Fig. 5-7, the percent COD removal efficiencies were inversely proportional to the initial TBC concentrations, and the higher the TBC concentration the lower the percent removal was. The residual COD (mg/L) reached the lowest level (approximately 50 mg/L) at or above 25 MPa. Correspondingly, the percent COD removal reached its highest levels when the pressure was higher than 25 MPa. However, there was not a significant decrease in the residual COD (mg/L) at 28 MPa, so 25 MPa appeared to be the optimum pressure that achieves the best treatment without unnecessarily increasing the energy consumption. In the previous experiments where there was no TBC in sludge, and 22 MPa was adequate to achieve the optimum treatment under similar operational conditions (Fig. 5-4). These results indicate that the addition of the recalcitrant TBC required a higher reactor pressure of 25 MPa to achieve a similar

level of treatment with SCWO.

### ***5.3.2.3 Effect of oxygen excess***

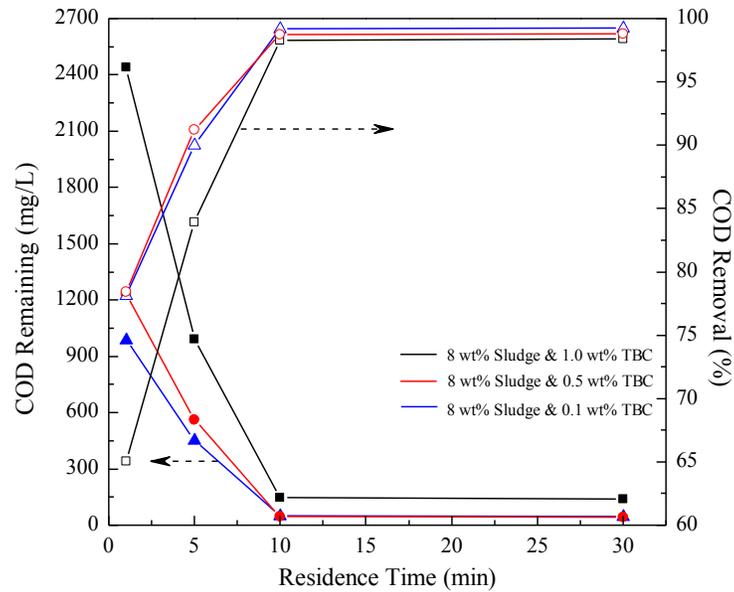
Fig. 5-8 shows the effect of oxygen excess on the SCWO treatment of 8 % sludge that was spiked with different concentrations of TBC. The temperature, residence time and pressure were kept constant at 550 °C, 10 min and 25 MPa, respectively, and n values of 1, 2, 3, 5, and 8 were applied in the experiments. The percent COD removal efficiencies were inversely proportional to the initial TBC concentrations, and higher TBC concentrations resulted in lower percent removals. The inflection point emerged at an oxygen excess of  $n = 3$ . A sharp decrease in COD was observed at  $n=2$ , and beyond  $n=3$  there was not a significant change in residual COD or percent COD removal. Since the price of hydrogen peroxide is not considered to be a significant expense, higher n values are preferred during operation to achieve the highest degradation possible, so 5 times of the oxygen excess was preferred.



**Fig. 5-8** Effect of oxygen excess on SCWO treatment of sludge spiked with TBC

**5.3.2.4 Residence time effects**

Fig. 5-9 shows the effect of residence time on the SCWO treatment of 8% sludge that was spiked with different concentrations of TBC. The temperature, oxygen excess, and pressure were kept constant at 550 °C, n=5, and 25 MPa, respectively. Residence times of 1, 5, 10 and 30 minutes were tested. As evident from Fig 6.9, a sharp decrease in residual COD was observed at 1 and 5 minutes, and the inflection point emerged at the point of 10 min. After 10 minutes, the residual COD (mg/L) was not improved significantly. Therefore, 10 min was regarded as the optimum residence time for sludge samples with TBC. Similar to the previous results, the percent COD removal efficiencies were inversely proportional to the initial TBC concentrations.



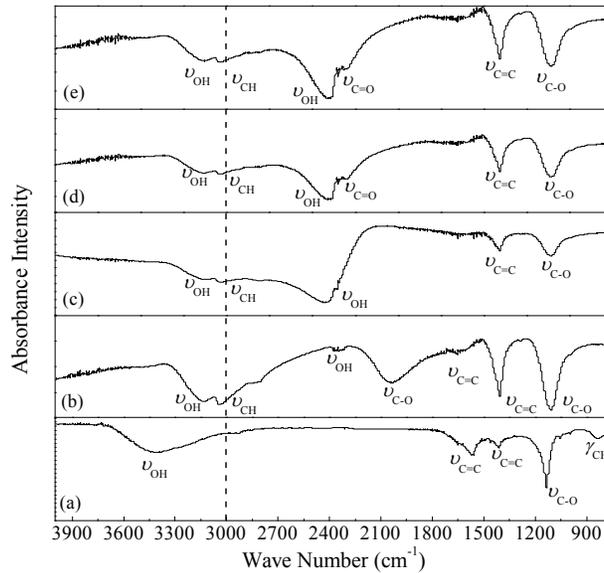
**Fig. 5-9** Effect of residence time on SCWO treatment of sludge spiked with TBC

Overall, these results showed that the concentration of TBC negatively affected the COD removal performance. In order to have a better understanding of the mechanisms involved and the changes in the microstructure of sludge, FTIR was employed.

### 5.3.3 FTIR results

Sludge samples with and without TBC were treated with SCWO at 550 °C, 25 MPa, 10 min and  $n = 5$ , and the samples were analyzed using FTIR before and after treatment. Fig. 5-10 (a) shows the IR spectrum of 8% sludge. The peaks around 3500  $\text{cm}^{-1}$  illustrate the vibration of the OH groups. This peak is not very to the interference from water molecules. The peaks at 1566  $\text{cm}^{-1}$  and 1410  $\text{cm}^{-1}$  are due to the C=C bond vibration, which indicates the presence of unsaturated hydrocarbons and their derivatives. The peak

at  $1130\text{ cm}^{-1}$  illustrates the emergence of C-O vibration and indicates that hydroxyl groups are mainly attached to the main carbon chain, such as alkanol and phenol, etc.



**Fig. 5-10** FTIR spectra of TBC spiked sludge after SCWO treatment. (a) 8 % sludge; (b) 8 % sludge with 0.5 % TBC; (c) 8 % sludge with 0.1 % TBC after SCWO degradation; (d) 8 % sludge with 0.5 % TBC after SCWO degradation; (e) 8 % sludge with 1.0 % TBC after SCWO degradation.

Fig. 5-10 (b) illustrates the IR spectrum of the sludge sample with 0.5% TBC. The results showed the emergence of the peak of the OH group vibration, which indicates that the hydrogen bond is generated abundantly because of the TBC addition. The OH groups on TBC can easily form hydrogen bonds with water molecules or water clusters. This phenomenon changes the degradation ability of the sludge matrix since the formation of hydrogen bonds increases the difficulty of sludge degradation. The peaks at  $1678\text{ cm}^{-1}$

and  $1405\text{ cm}^{-1}$  represent the benzene rings, and the peak at  $1105\text{ cm}^{-1}$  represents that the OH groups attached to the benzene ring. The peak at  $1105\text{ cm}^{-1}$  is also due to the 1, 2, 4-substitution on the benzene ring.

Fig. 5-10 (c), (d) and (e) illustrate the changes in the IR spectra and degradation after SCWO treatment of sludge samples containing 0.1, 0.5 and 1% TBC. Strong peaks at  $2415\text{ cm}^{-1}$  with large areas were observed which indicated the attachment of OH to the C=O groups. This means that the alkanol compounds and phenol compounds are mainly oxidized into short-chain organic acids. The vibration of C=O bond at  $2296\text{ cm}^{-1}$  indicates the  $\text{CO}_2$  generation, which can also be used to evaluate the extent of the oxidation reactions.

The FTIR characterization illustrates the interaction between TBC and sludge matrix and the effects on the degradation of the sludge matrix. These results indicate that the TBC addition increases the difficulty of sludge degradation because of the formation of hydrogen bonds, and support the experimental results presented in figures 5-6~5-9 that show lower COD removals with increasing TBC concentrations. Additionally, the p-tert-butyl group also appears to influence the degradation of sludge because of the steric effect which decreases the possibility of collisions between sludge constituents and  $\text{H}_2\text{O}_2$  molecules.

## 5.4 CONCLUSION

This study investigated the performance of the SCWO treatment for wastewater sludge and the degradation of TBC under a range of operational conditions including reactor temperature, pressure, oxygen excess and residence time. The results showed that increasing the reactor temperature, pressure, oxygen excess and residence time increases the COD removal and treatment performance. However, beyond a certain point, no additional benefits are observed. Therefore it is important to optimize the operational conditions to maximize the treatment capability and minimize the energy needs. The optimum initial sludge solid content of sludge was found to be in the range of 8-10 %, and the optimum operational parameters were 550 °C, 25 MPa and an oxygen excess of 5. Over 99 % COD removal could be achieved under these conditions. The addition of TBC (0.1, 0.5, and 1 %) affected the efficiency of sludge degradation. As the TBC concentration was increased, it resulted in lower percent COD removal likely due to the formation of hydrogen bonds, increase in viscosity, increase in steric hindrance and decrease in the probability of collisions between the organic compounds and oxidants. Regardless of this, over 98 % COD removal was achieved for all samples containing TBC under typical operational conditions with final COD values less than 50 mg/L. This shows the effectiveness of the SCWO process for sludge treatment, and sludge treated with SCWO can be safely discharged to the environment without causing any concerns for public health or the environment.

## **Acknowledgment**

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## CHAPTER 6

### 6 Summary and Conclusions

In Phase 1, the effect of temperature on sludge conditioning was studied, and the polymer dose was optimized at different temperatures. Thickening and dewatering performance was investigated at 10 °C, 35 °C, 50 °C, 60 °C, and 100 °C using filtration, capillary suction time (CST), settling tests and zeta potential measurements. A high molecular weight and medium-high cationic charge polyacrylamide (PAM) polymer (Zetag 8160) was used to condition sludge. As conclusions in *Phase I*, the temperature was found to be an important factor that impacts sludge conditioning, optimum polymer dose, and thickening and dewatering performance. A wide range of sludge temperatures (10 °C, 35 °C, 50 °C, 60 °C and 100 °C) were tested. In the temperature range of 10 °C to 50 °C, the polymer dose required for conditioning was similar but resulted in different thickening and dewatering performance. The best results were observed at 50 °C, where the highest filtrate volume, cake solids, and settling velocity were obtained at a polymer dose of 19.2 g/kg DS. Thickening and dewatering performance was also good at 35 °C. Increasing the sludge temperature further increased the polymer demand up to 38.5 g/kg DS and deteriorated the thickening and dewatering performance. The results of this research show that sludge conditioning at 35~50 °C can significantly improve treatment performance and result in savings for treatment plants. There would be no additional cost for heating sludge at wastewater treatment plants where thermal treatment processes (e.g.,

supercritical water oxidation, thermal hydrolysis, wet oxidation, etc.) are used.

Phase 2 investigated the performance of the SCWO treatment for wastewater sludge and the degradation of TBC under a range of operational conditions including reactor temperature, pressure, oxygen excess and residence time. The results showed that increasing the reactor temperature, pressure, oxygen excess and residence time increases the COD removal and treatment performance. However, beyond a certain point, no additional benefits are observed. Therefore it is important to optimize the operational conditions to maximize the treatment capability and minimize the energy needs. The optimum initial sludge solid content of sludge was found to be in the range of 8-10 %, and the optimum operational parameters were 550 °C, 25 MPa and an oxygen excess of 5. Over 99 % COD removal could be achieved under these conditions. The addition of TBC (0.1, 0.5, and 1 %) affected the efficiency of sludge degradation. As the TBC concentration was increased, it resulted in lower percent COD removal likely due to the formation of hydrogen bonds, increase in viscosity, increase in steric hindrance and decrease in the probability of collisions between the organic compounds and oxidants. Regardless of this, over 98 % COD removal was achieved for all samples containing TBC under typical operational conditions with final COD values less than 50 mg/L.

The results of this study show the high effectiveness of the SCWO process for sludge

treatment and successful degradation of recalcitrant compounds. Sludge treated with SCWO can be safely discharged to the environment without causing any significant concerns for public health or the environment.

## CHAPTER 7

### 7 Recommendations for Future Study

Based on the findings of this study, the following recommendations are made for future studies on the SCWO treatment of sludge:

*i.* Continuous SCWO reactors should be tested for sludge treatment. So far, most of the reactors used for sludge treatment were batch reactors. Continuous reactors can expand the daily capacity of the SCWO treatment, and more lab-scale studies are needed to explore the performance of the SCWO reactors.

*ii.* The molecular mechanisms of the SCWO on sludge treatment were difficult to analyze without the in-situ characterization. The high reactor temperature and pressure was a challenge for in-situ characterization. Therefore, to develop novel characterization approach which can suffer from the critical conditions is meaningful and helpful.

*iii.* To understand the mechanisms of the degradation of organic compounds, molecular modeling of the SCWO process should be conducted by choosing a wide range of organic compounds with different chemical properties. The modeling should include the degradation mechanisms of single organic compounds and the interactions between

different species of organic compounds.

*iv.* SCWO can convert all of the organic matter into their final oxidized state, i.e. CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>3</sub><sup>-</sup> etc. However, SCWG (supercritical water gasification, no oxidants) and SCWPO (supercritical water partial oxidation, oxygen excess < 1) can convert some of the organic matter into biogas, i.e. H<sub>2</sub>, CH<sub>4</sub>, and CO, etc., which may also have potential applications for sludge treatment, and can be favourable for energy recovery and generation.

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