



A kinetic model of municipal sludge degradation during non-catalytic wet oxidation



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ABSTRACT

Wet oxidation is a successful process for the treatment of municipal sludge. In addition, the resulting effluent from wet oxidation is a useful carbon source for subsequent biological nutrient removal processes in wastewater treatment. Owing to limitations with current kinetic models, this study produced a kinetic model which predicts the concentrations of key intermediate components during wet oxidation. The model was regressed from lab-scale experiments and then subsequently validated using data from a wet oxidation pilot plant. The model was shown to be accurate in predicting the concentrations of each component, and produced good results when applied to a plant 500 times larger in size. A statistical study was undertaken to investigate the validity of the regressed model parameters. Finally the usefulness of the model was demonstrated by suggesting optimum operating conditions such that volatile fatty acids were maximised.

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1. Introduction

Municipal sludge is the semi-solid residue remaining at the end of a municipal wastewater treatment process. The treatment of municipal sludge is becoming increasingly important as current disposal methods such as landfill are not sustainable, Gómez et al. (2005), and regulations surrounding sludge disposal are becoming more restrictive, (an indicative example being Potts (2003)). This is intensifying the search for alternative disposal and treatment processes that can address the unique challenges that municipal sludge present, in particular the high water content and the presence of pathogens.

One attractive wastewater treatment alternative is wet oxidation. Wet oxidation is the liquid phase treatment of organic or oxidisable inorganic compounds at elevated temperature and pressure, typically using oxygen as an oxidant (applied as air or pure oxygen gas). The typical range of reaction conditions for wet oxidation are 150–320 °C at 20–150 bar of pressure and a residence time of 15–120 min Zou et al. (2007). A historical review of wet oxidation for the treatment of pulp mill liquors and subsequently

for wastewater sludge treatment over the last 40 years is given in Debellefontaine and Foussard (2000).

Given that wet oxidation does not require water removal prior to treatment, it can directly process liquid municipal sludge. Furthermore the high temperatures involved kill the pathogens present and sterilise the material. While the wet oxidation process has been the focus of numerous studies Van Amstel and Rietema (1973); Li et al. (1991); Mishra et al. (1995); Debellefontaine and Foussard (2000), there are still relatively few models that describe the kinetic behaviour of the intermediate and final products of municipal sludge under different reaction conditions needed for an in-depth process analysis.

The first stage in the wet oxidation of sludge involves a large proportion of the insoluble organic content being solubilised through hydrolytic depolymerisation. Subsequent oxidative reactions convert these hydrolysis products into increasingly simpler organics such as acetic acid and formic acid, and acetone and ash. Finally these products can be further oxidised to CO₂, water and residual ash, Bernardi et al. (2010); Debellefontaine and Foussard (2000).

The reaction pathways that occur under wet oxidation are complex and poorly characterised. Even wet oxidation of pure substances such as phenol have been shown to decompose via numerous reaction pathways, and therefore it is necessary to use a

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simplified kinetic model which only includes the dominant reaction pathways [Moreno et al. \(2012\)](#); [Zhang and Chuang \(1999\)](#). Because of this, simplified lumped kinetic models, often employing pseudo-components such as Chemical Oxygen Demand (COD) in the kinetic model, are used to conveniently describe the wet oxidation process.

The variety of previously proposed lumped parameter models for the wet oxidation of a range of waste products, (including municipal sludge) is evident from the range of models listed in [Table 1](#). [Van Amstel and Rietema \(1973\)](#) was one of the first to propose a lumped model for municipal sludge. This early work was further expanded by other researchers [Foussard et al. \(1989\)](#); [Li et al. \(1991\)](#); [Khan et al. \(1999\)](#); [Shanableh \(2004\)](#) who investigated different operating conditions and proposed modifications to the kinetic pathways. [Li et al. \(1991\)](#) proposed the familiar generalised lumped kinetic model for municipal sludge which forms the basis for the development of the kinetic model proposed in this work.

Historically, the primary outcome of wet oxidation applied to municipal waste was complete oxidation to the final end products which are mainly CO₂, water and residual solids, [Mishra et al. \(1995\)](#). However with wastewater treatment plants incorporating Biological Nutrient Removal (BNR) facilities becoming more common, the short chain acids which are an intermediate product of wet oxidation, can be used as an effective carbon source for the denitrifying bacteria, [Djafer et al. \(2000\)](#); [Shanableh and Jomaa \(2005\)](#); [Strong et al. \(2011\)](#); [Andrews et al. \(2014\)](#); [Baroutian et al. \(2015\)](#).

While models like that proposed by [Li et al. \(1991\)](#) give information on the rate of solids or COD reduction and acetic acid production, they generally lack detailed modelling of the intermediate products produced, such as the fate of nitrogen based compounds. The additional load of these intermediate products in the liquid effluent produced by a wet oxidation facility has the potential to upset downstream biological treatment processes. This provides the motivation to develop a more comprehensive model that can better predict the fate of these intermediate compounds.

Despite the fact that wet oxidation liquor is a useful supplement for a BNR treatment plant, and generalised kinetic models of wet oxidation are available, none of the dynamic models in [Table 1](#) adequately describe the spectrum of intermediate products, and the conditions under which they are produced. Consequently there is a need for more detailed kinetic models describing wet oxidation which characterise sufficiently the concentrations of the intermediate compounds, such that potential impact on a downstream biological treatment plant can be predicted. Therefore, this paper proposes a detailed kinetic model for wet oxidation of municipal sludge which can predict the concentration of intermediate products which are important to BNR processes under different reaction conditions.

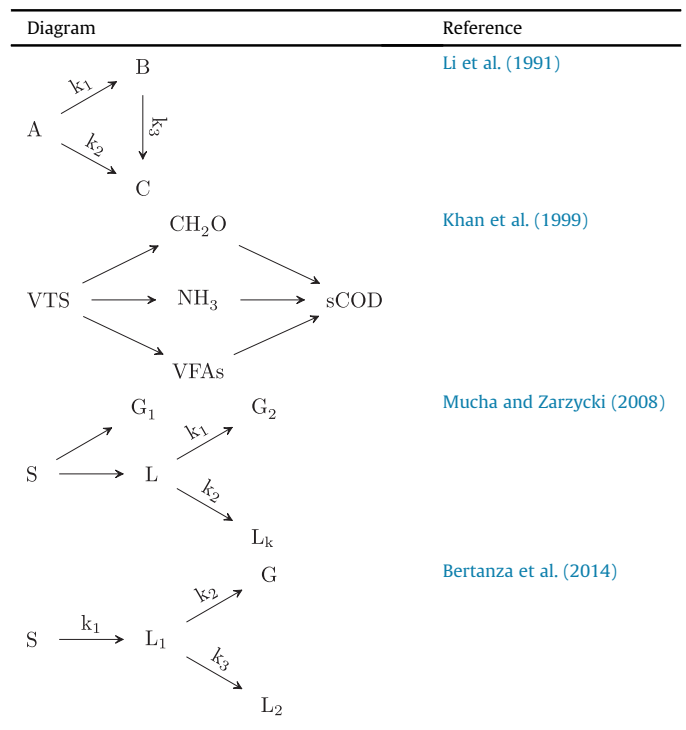
Table 1

Summary of published wet oxidation kinetic models. (See also [Table 2](#).)

Investigators	Feed material	Model inputs	Reaction pathways	Validated states
Takamatsu et al. (1970)	Mixture of peptone, glucose & metal salts	O ₂ , T	3	3
Van Amstel (1971)	Municipal sludge	O ₂ , T, P	2	1
Foussard et al. (1989)	Municipal sludge	O ₂ , T	2	1
Li et al. (1991)	Municipal sludge	O ₂ , T	3	1
Khan et al. (1999)	Municipal sludge	O ₂ , T	4	4
Zhang and Chuang (1999)	Kraft pulp sludge	O ₂ , T	2	1
Verenich and Kallas (2002); Verenich et al. (2003)	Pulp mill liquor	O ₂ , T	4	1
Shanableh (2004)	Municipal sludge	O ₂ , T	2	2
Chacuk and Imbierowicz (2007)	Municipal sludge	O ₂ , T	4	0
Mucha and Zarzycki (2008)	Municipal sludge	T	4	1
Bertanza et al. (2014)	Municipal sludge	O ₂ , T	3	2
<i>This work</i>	Municipal sludge	O ₂ , T, P, RPM	12	7

Table 2

Comparison of published wet oxidation kinetic pathways.



[Table 2](#) compares the kinetic structure of the key lumped kinetic models noted in [Table 1](#) starting with the basic [Li et al. \(1991\)](#) model similar to that presented in ([Bertanza et al., 2014, Table 3](#)). In all models, the variable k_i is an Arrhenius based rate expression. The species symbols used are the same as the original references. In the models presented by [Mucha and Zarzycki \(2008\)](#) and [Bertanza et al. \(2014\)](#), S are the feedstock particular organic compounds, L, L_1 are intermediate liquid products, and G_i and L_k, L_2 refers to gaseous and non biodegradable liquid products respectively. It is clear from the topology that while they may appear different, from a mechanistic viewpoint they are related, and descend from the Li et al. model. Each model starts with an initial compound which is degraded or solubilised to an intermediate product. This is then oxidised to one or more reaction end products. For comparison, the model presented in this work is given in [Fig. 3](#).

However there are some deficiencies of these mechanistic models which was the motivating factor to develop a more comprehensive model and to undertake experiments to investigate the effect of temperature, oxygen partial pressure and mixing in the form of stirrer speed, on the degradation of biosolids under

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