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Determination of the Relationship between the Energy Content of Municipal Wastewater and its Chemical Oxygen Demand

Ziye Dai, Elizabeth S. Heidrich*, Jan Dolfing and Adam P. Jarvis

School of Engineering, Newcastle University, Newcastle upon Tyne NE1 7RU, UK.

***Corresponding Author** E-mail: elizabeth.heidrich@ncl.ac.uk. Tel: +44 (0)191 208 8997. Fax: +44 (0)191 208 6502

Abstract

Quantitatively evaluating progress towards energy neutral, or even energy positive, wastewater treatment necessitates reliable data on the intrinsic energy content of the wastewater. It has long been assumed that the amount of energy in wastewater is directly related to its chemical oxygen demand (COD), but the convoluted method for measuring the wastewater energy content has meant that a reliable, statistically robust relationship between COD and energy has never been drawn. In this research we use a new drying method and analysed a set of 107 municipal wastewater samples, with a range of COD values from 16.4 to 1151 mg/L. The results revealed a strong correlation between COD and energy content of 16.1 kJ/g COD ($p < 0.001$). Reliable predictions of a wastewater's energy content can now be made on the basis of the COD measurement alone.

Keywords:

Energy, wastewater, COD, ammonia

1. Introduction

It has been estimated that municipal wastewater treatment accounts for approximately 3 – 5% of total global energy usage [1,2]. Demand for wastewater treatment has increased dramatically in recent years in major economies such as China [3], and in many parts of the world standards for treated effluent discharge are becoming more stringent [4]. Thus, whilst there is a pressing need to reduce energy consumption globally to combat the effects of climate change, the municipal wastewater treatment sector faces substantial challenges in contributing to this effort.

Common municipal wastewater treatment technologies such as the activated sludge process have substantial energy requirements, especially due to aeration, which accounts for approximately 50% of the total process energy demand [5]. Despite this high energy consumption current estimates suggest that there is four to five times more energy in wastewater than is used to operate wastewater treatment plants [4,5]. This implies that if energy consumption is reduced and energy recovery maximised it should be feasible for wastewater treatment to be at least energy neutral [4] or even energy positive [6].

Quantitatively evaluating progress towards energy neutral, or energy positive, wastewater treatment necessitates reliable data for both energy consumption and the intrinsic energy content of the wastewater. The energy content of wastewater comes primarily from compounds that contribute to Chemical Oxygen Demand (COD) such as lipids and carbohydrates; the contributions of nitrogen compounds (0.3 kWh/m^3) are a relatively minor component (~ 15%) of the total theoretical energy content of 1.96 kWh/m^3 [5].

Chemical Oxygen Demand (COD) is therefore taken to be indicative of the energy content of wastewater since it broadly quantifies the amount of energy-containing organic matter within it. The advantage of using COD as a measure of energy content is that it is among the most commonly determined properties of municipal wastewater, its analysis is a straightforward procedure. But the relationship between COD and energy content is very poorly defined.

The reason for the poor comprehension of the relationship between COD and energy content is that accurate measurement of the energy content of wastewater has been hampered by the methods available for its determination. In particular, the difficulties arise because of the need to dry relatively large volumes of aqueous sample prior to determination of the energy content, by bomb calorimetry, on the dried residue [7,8]. Shizas and Bagley [7] accomplished this via oven drying at 103°C but, whilst a relatively quick drying procedure, oven drying will have driven off the volatile organic compounds that are a key contributor to the overall energy content of the wastewater. Heidrich et al. [8] measured COD losses during oven-drying of 44 – 49%, and therefore developed a freeze-drying method to avoid such losses. This approach reduced COD loss to 18 – 25% but the main problem with this method was that the drying procedure took four to eight weeks for a single sample.

Korth et al.[9] gathered samples from two wastewater treatment sites over the course of one year, each sample taken at the same time in the morning. The authors acknowledge the advantage of capturing more of the energy containing compounds using the state of the art method of freeze drying, but due to the time requirement of this method it was only used for three of the samples taken. These had an average energy of 13.0 kJ/gCOD, capturing substantially more energy than the 14 oven dried samples of 5.9 kJ/gCOD. Though this study adds three more data values for the amount of energy in wastewater, the relationship with COD remains elusive.

If the energy content of wastewater is to be routinely used in understanding performance efficiencies of energy yielding treatment processes such as the use of anaerobic digestion or the use of bioelectrochemical systems, there needs to be either: a substantially easier method of making this measurement; or a robust and significant link between the energy and another easy to measure parameter, most likely the COD. The former option is unlikely as total energy content must be measured by bomb calorimetry, which in itself uses a specialised piece of equipment, and further to this the sample of wastewater must be dried prior to this analysis, and the drying process can greatly affect the energy content. The objectives of this investigation were to (i) develop a more efficient, but accurate, method for the determination of the energy content of wastewaters and (ii) reliably determine the relationship between COD and energy content of municipal wastewater.

2. Materials and Methods

2.1. Sample collection and study sites

Samples were collected between March and October 2016 from four municipal wastewater treatment plants with varying population equivalents. In total 62 composite samples and 48 spot samples were taken. (Details in Supporting Information S1). At the request of the wastewater treatment companies the plants from which samples were collected have been anonymised. All four of the UK wastewater treatment plants (Wastewaters A, B, C and D) comprise mechanical settlement as the primary treatment process followed by secondary treatment using the activated sludge process. There was a 25-fold difference in population equivalents served between the smallest and the largest plant, and the plants are distributed over a wide geographical area of Northern England and Scotland. During the site selection process plants involving high levels of industrial effluent were avoided, as previous research has shown these are more likely to contain high energy containing compounds which will distort the results [8]. The WWTPs chosen mainly treat domestic wastewater with less than 10% of industrial trade effluent.

2.2. Drying method

To avoid problems with substantial energy losses due to oven drying, or very long drying times by freeze-drying [8], in this new method samples were dried using a Genevac Rocket 4D Synergy centrifugal evaporator (SP Scientific, Warminster, Pennsylvania, USA). Glass drying flasks for the centrifugal evaporator were first dried at 104°C for 1 hour, cooled to room temperature in a desiccator, and weighed. The apparatus allowed for six glass drying bottles with 400ml capacity to be dried simultaneously. On each run 2 independent samples of wastewater were prepared, for each wastewater, two flasks were used to yeild enough mass to use for the bomb calorimeter, and one flask used for the determination of the COD losses during drying. The optimal drying conditions were determined experimentally to 18 mbar pressure, 30°C and 1800 rpm for 18 hours and 40 minutes, these were used throughout. Once drying was complete the flasks were further dried in a desiccator for at least two days until the flask and its contents reached constant weight. The weight of the flask was subtracted from the weight of the flask plus dried contents to yield total solids concentration of the sample by centrifugal evaporation (TS_{ce}).

2.3. Chemical and energy analysis

Chemical analysis of the raw wastewater samples was carried out within 48 hours of sample collection. The energy content of the dried sample was conducted using standard calorimetric methods with a Parr 6100 Compensated Jacket Bomb Calorimeter (Parr Instrument Company, Moline, Illinois, USA). (Details in Supporting Information S1). The drying method above yielded approximately 0.5g of sample per wastewater which was then mixed with a measured quantity of paraffin wax which acts as a combustion aid to allow complete combustion of the sample. Prior to the analysis wastewater samples, rigorous method development of the drying and combustion methods was completed which showed the low variability among replicas with this method (Supporting Information SI 1.4 and Table S2). A strategic decision was made to complete the analysis of 107 independent repeat samples, rather than a lower number of independent repeats but with replication (i.e. 36 triplicate samples). Replicates are not an independent test of a hypothesis and do not therefore provide reproducibility of the main result, they cannot be used to generate P values [10]. Previous research [11] used 38 triplicate samples and was not able to show a statistically significant correlation of energy with wastewater parameters. The inherent heterogeneity of wastewater means that large sample sizes are needed to draw statistically robust conclusions.

2.4. COD and energy losses during drying

To measure COD loss using centrifugal evaporation 40 mL of each wastewater sample was dried simultaneously alongside the samples for the energy analysis, it was subjected to the same drying times and forces. A lower volume (40ml rather than 400ml) was used as the dried sample was very difficult to rehydrate into a homogenous solution. After drying, 40 mL of deionised water was introduced to the drying flask which was then placed in a sonication bath for 10 minutes to aid complete rehydration of the dried sample. COD was then measured on the sample using the same standard procedure as for the original wastewater sample. Thus, percentage COD loss could be calculated. Original COD ($COD_{original}$) and rehydrated COD ($COD_{rehyd.}$) was measured on 36 individual wastewater samples, with triplicate analysis of COD on both original wastewater samples and rehydrated samples in all cases.

2.5. Data analysis

Summary statistics were computed in Excel 2013. Minitab 17 was used to calculate Spearman's rank correlation coefficient (r_s) and significance levels (p) for these non-normally distributed data.

3. Results and Discussion

There is a strong positive linear relationship between COD and energy content of municipal wastewater (Figure 1). The correlation between COD and energy content is strongest for the composite samples ($r_s = 0.967$, $p < 0.001$, n = 62; Figure 1A), and the regression line indicates an energy value of 16.1 kJ/g COD. Calculating the regression equation for the spot samples gives an energy content value of 15.6 kJ/g COD ($r_s = 0.855$, $p < 0.001$, n = 48; Figure 1B). Taking all the data collected yields an energy value of 15.8 kJ/g COD ($r_s = 0.916$; $p < 0.001$, n = 107; Figure 1C). Wastewater is highly variable with changes in composition, strength and therefore energy over any 24 hour period, creating greater scatter in the data points particularly at low COD values (See Figure S1 in SI). Composite samples are collected and averaged over 24 hours, the value of 16.1 kJ/g COD using these samples is therefore more statistically robust.

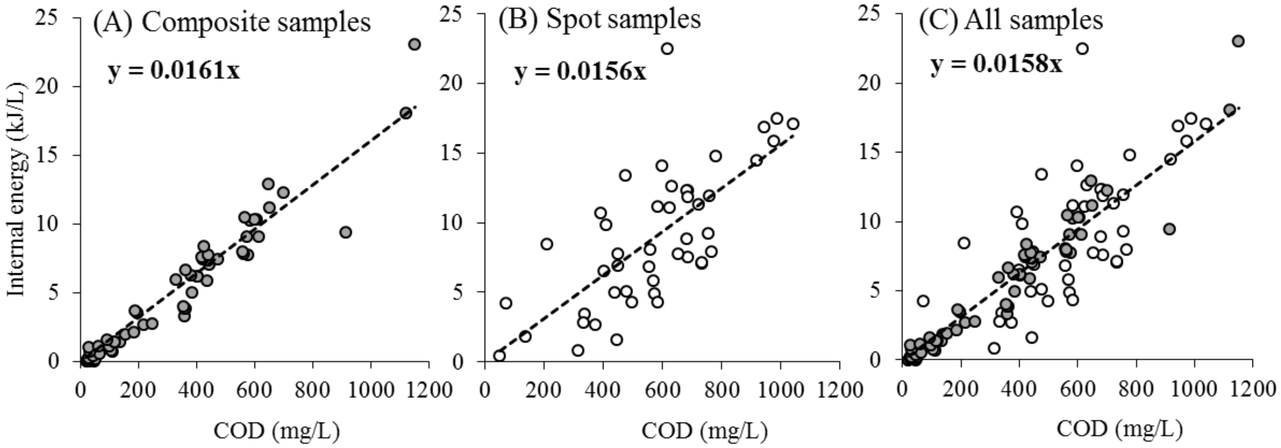

Figure 1. The relationship between COD and energy content of municipal wastewater for (A) composite samples, (B) spot samples and (C) all samples. The line of best fit is put through the origin in all graphs on the basis that COD is used as an indicator of wastewater composition; zero COD therefore indicates zero energy, further graphs with an intercept are shown in S2 in SI.

The relationship between COD and energy content has been determined from analyses of municipal wastewaters of varying strength with respect to COD, but the four municipal wastewaters sampled are typical of COD concentrations of municipal wastewaters internationally 430 mg/L to 800 mg/L for medium and high strength wastewaters respectively [12].Summary statistics for the quality of the four wastewaters are shown in Table S2 (Supporting Information). Mean COD concentrations (± standard deviation) ranged from 378.9 ± 174.3 mg/L in Wastewater D to 684.8 ± 198.0 mg/L in Wastewater B, with an overall mean (all raw wastewaters) of 552.3 ± 239.7 mg/L (*n* = 72). Primary treated effluent wastewater had mean COD concentrations ranging from 150.0 ± 55.9 mg/L to 450.0 ± 96.2 mg/L (overall mean of all wastewaters of 326.1 ± 147.0

mg/L (n = *20*)), and mean secondary treated COD concentrations ranged from 24.9 ± 6.7 mg/L to 93.8 ± 27.4 mg/L (overall mean of all wastewaters of 45.8 ± 30.2 mg/L (*n* = 24)).

The large sampling effort of 107 wastewater samples was facilitated by the improved drying method of centrifugal evaporation. This method of evaporation is used in chemical and biochemical laboratories as a gentle yet efficient means of removing liquids or solvents form a small sized samples. Larger capacity units, such as the one used in this study, are now also used in the high end catering industry to produce highly reduced sauces. Results showed that the centrifugal evaporation drying of samples has a greater COD recovery than both freeze-drying and oven-drying (see Table 1). Using the centrifugal evaporation drying process there was no particular difference in COD loss during drying of raw wastewater, primary treated and final effluent, despite the large differences in initial COD: 87.4%, 82.6% and 82.9% respectively (see Table 1). Losses of COD during drying have previously been ascribed to loss of volatile organic compounds such as acetate [8], and that may be the case with losses during centrifugal evaporation drying also. Nevertheless, centrifugal evaporation incurs lower losses, and is also a quicker drying process than freeze-drying taking approximately 3 days to dry up to 2.4 L of wastewater sample as compared to 28 days to freeze dry 1.5 L [8].

Table 1. COD Concentrations of Original Wastewater Samples and Rehydrated Samples, and Percentage COD Recovery, Using Different Drying Methods

drying method	number of separate wastewater aliquots	$COD_{original}$	COD_{rehyd}	mean COD recovery (%)
centrifugal evaporation	36[A]	309.9 ± 307.2	267.1 ± 279.7	84.8%
freeze-drying[13]	2[B]	647.3 ± 25.5	506.2 ± 24.4	77.8%
oven-drying[13]	2[B]	647.3 ± 25.5	346.1 ± 15.2	53.7%

[A] A randomised selection of raw wastewater (*n* = 16), primary treated effluent (*n* = 12) and final effluent (*n* = 8); mean and standard deviation calculated from measured values of all 42 samples.

[B] Data from Ref[8]; mean and standard deviations are calculated from triplicate analyses of two single samples of wastewater

Previous thermodynamic calculations have shown that the energy content of a wide variety of organic compounds range from approximately 13 – 17 kJ/g COD [8]. Table 2 shows calculated values for the energy content of a selection of organic compounds commonly found in municipal wastewaters [14]. The energy per gram of COD in these compounds is typically a little lower than that of the measured values of wastewaters (Figure 1).

This may be because there are constituents of wastewater which may contribute to the energy content but not the COD, most notably urea (enthalpy of combustion of -632 kJ/mol [15]. Scherson and Criddle [5] theoretically estimate the contribution of different compounds to the total energy content of wastewater. They approximate nitrogen based compounds to account for 15% of the total energy, COD based compounds accounting for the remaining 85%. The total energy measured by bomb calorimetry is representative of the energy in the COD and the energy in the nitrogen based compounds (less the amount which has been volatilised during the drying process). If the COD is only 85% of this, then the true value of energy per gram of COD is 13.7 kJ/gCOD. This falls well within the range of known organic compounds shown in table 2. When TKN as a measure of nitrogen based compounds was added into the regression, there was an inconsequential improvement in the correlation producing an r^2 value of 93.2%, compared to r^2 of 92.9% with COD alone (details in SI ***) . COD acts as a good proxy for both these measurements.

Table 2 Common Organic Compounds and their Calculated Energy Values

compounds[a]	**type**	**formula**	**ΔH kJ/gCOD**[b]
glutamic acid	proteins	$C_5H_9NO_4$	13.4
aspartic acid		$C_4H_7NO_4$	13.3
glucose	sugars	$C_6H_{12}O_6$	14.6
xylose		$C_5H_{10}O_5$	14.7
acetic acid	volatile fatty acids	CH_3COOH	13.6
butyric acid		$CH_3CH_2CH_2COOH$	13.6
fulvics	humic substances	$C_{33}H_{32}O_{19}$	15.7
humics		$C_{34}H_{34}O_{16}N_2$	11.6-14.5
cellulose	others	$(C_6H_{12}O_6)_n$	14.6
lignin		$(C_9H_{10}O_2)_{n,}$ $(C_{10}H_{12}O_3)_n$ or $(C_{11}H_{14}O_4)_n$	14.1

[a] A selection of different compound types selected, but all have been shown to be present at high concentration in municipal wastewater by Huang et al. [14].

$^{b}\Delta H$ (kJ/gCOD) is calculated from deoxygenation enthalpy values presented by Sato [16], except for Fulvics which is based on data in Reddy *et al.* [17]. Values for energy content of additional organic compounds can be found in Heidrich *et al.* [8].

Multiple regression analysis was used to determine the relationship between energy content and all the wastewater parameters tested: COD, pCOD, TOC, DOC, VS, $N\text{-}NH_4^+$ and $P\text{-}PO_4^{3-}$ (see Supporting Information S4 and S5). The parameters related directly to COD show a good correlation with energy, $N\text{-}NH_4^+$ and $P\text{-}PO_4^{3}$ are found to have no statistical correlation with energy. The use of multiple variables within the regression analysis does not improve the model beyond the use of COD alone. Within municipal wastewater COD can be regarded as a good proxy for the concentration of all constituents. The value of 16.1 kJ/gCOD is therefore an empirical mathematical factor of how much energy there is in wastewater per g of COD material it contains, rather than the true relationship of how many kJ of energy is actually in each gram of COD.

The comprehensive and rigorous analysis of the amount of energy within wastewater has yielded the statistically significant relationship between COD and energy content of 16.1 kJ/gCOD. Using this, a reliable estimate of any wastewater's energy content can now be made from the simple measurement of COD. This strategically important value will assist in the development of energy mass balances for wastewater treatment plants, which will in turn support efforts to transform such systems into energy neutral, or even energy positive, operations.

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Supporting Information

Supporting information is provided on the methods, chemical characteristics of the four wastewaters, variability in the data set and regression analysis of different wastewater properties with energy.

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