

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

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10

11 **Abstract**

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

22

23 **Keywords:**

24 Energy, wastewater, COD, ammonia

25 **1. Introduction**

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

32
33 Common municipal wastewater treatment technologies such as the activated sludge process
34 have substantial energy requirements, especially due to aeration, which accounts for approximately
35 50% of the total process energy demand ⁵. Despite this high energy consumption current estimates
36 suggest that there is four to five times more energy in wastewater than is used to operate
37 wastewater treatment plants ^{4,5}. This implies that if energy consumption is reduced and energy
38 recovery maximised it should be feasible for wastewater treatment to be at least energy neutral ⁴
39 or even energy positive ⁶.

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41 Quantitatively evaluating progress towards energy neutral, or energy positive, wastewater
42 treatment necessitates reliable data for both energy consumption and the intrinsic energy content
43 of the wastewater. The energy content of wastewater comes primarily from compounds that
44 contribute to Chemical Oxygen Demand (COD) such as lipids and carbohydrates; the contributions
45 of nitrogen compounds (0.3 kWh/m³) are a relatively minor component (~ 15%) of the total
46 theoretical energy content of 1.96 kWh/m³ ⁵.

47

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

53
54 The reason for the poor comprehension of the relationship between COD and energy
55 content is that accurate measurement of the energy content of wastewater has been hampered by
56 the methods available for its determination. In particular, the difficulties arise because of the need
57 to dry relatively large volumes of aqueous sample prior to determination of the energy content, by
58 bomb calorimetry, on the dried residue ^{7,8}. Shizas and Bagley ⁷ accomplished this via oven drying
59 at 103°C but, whilst a relatively quick drying procedure, oven drying will have driven off the
60 volatile organic compounds that are a key contributor to the overall energy content of the
61 wastewater. Heidrich et al. ⁸ measured COD losses during oven-drying of 44 – 49%, and therefore
62 developed a freeze-drying method to avoid such losses. This approach reduced COD loss to 18 –
63 25% but the main problem with this method was that the drying procedure took four to eight weeks
64 for a single sample.

65
66 Korth et al. ⁹ gathered samples from two wastewater treatment sites over the course of one
67 year, each sample taken at the same time in the morning. The authors acknowledge the advantage
68 of capturing more of the energy containing compounds using the state of the art method of freeze
69 drying, but due to the time requirement of this method it was only used for three of the samples
70 taken. These had an average energy of 13.0 kJ/gCOD, capturing substantially more energy than

71 the 14 oven dried samples of 5.9 kJ/gCOD. Though this study adds three more data values for the
72 amount of energy in wastewater, the relationship with COD remains elusive.

73

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

85

86 **2. Materials and Methods**

87

88 *2.1. Sample collection and study sites*

89 Samples were collected between March and October 2016 from four municipal wastewater
90 treatment plants with varying population equivalents. In total 62 composite samples and 48 spot
91 samples were taken. (Details in Supporting Information S1). At the request of the wastewater
92 treatment companies the plants from which samples were collected have been anonymised. All
93 four of the UK wastewater treatment plants (Wastewaters A, B, C and D) comprise mechanical

94 settlement as the primary treatment process followed by secondary treatment using the activated
95 sludge process. There was a 25-fold difference in population equivalents served between the
96 smallest and the largest plant, and the plants are distributed over a wide geographical area of
97 Northern England and Scotland. During the site selection process plants involving high levels of
98 industrial effluent were avoided, as previous research has shown these are more likely to contain
99 high energy containing compounds which will distort the results ⁸. The WWTPs chosen mainly
100 treat domestic wastewater with less than 10% of industrial trade effluent.

101 *2.2. Drying method*

102 To avoid problems with substantial energy losses due to oven drying, or very long drying
103 times by freeze-drying ⁸, in this new method samples were dried using a Genevac Rocket 4D
104 Synergy centrifugal evaporator (SP Scientific, Warminster, Pennsylvania, USA). Glass drying
105 flasks for the centrifugal evaporator were first dried at 104°C for 1 hour, cooled to room
106 temperature in a desiccator, and weighed. The apparatus allowed for six glass drying bottles with
107 400ml capacity to be dried simultaneously. On each run 2 independent samples of wastewater were
108 prepared, for each wastewater, two flasks were used to yeild enough mass to use for the bomb
109 calorimeter, and one flask used for the determination of the COD losses during drying. The optimal
110 drying conditions were determined experimentally to 18 mbar pressure, 30°C and 1800 rpm for 18
111 hours and 40 minutes, these were used throughout. Once drying was complete the flasks were
112 further dried in a desiccator for at least two days until the flask and its contents reached constant
113 weight. The weight of the flask was subtracted from the weight of the flask plus dried contents to
114 yield total solids concentration of the sample by centrifugal evaporation (TS_{ce}).

115

116 *2.3. Chemical and energy analysis*

117 Chemical analysis of the raw wastewater samples was carried out within 48 hours of
118 sample collection. The energy content of the dried sample was conducted using standard
119 calorimetric methods with a Parr 6100 Compensated Jacket Bomb Calorimeter (Parr
120 Instrument Company, Moline, Illinois, USA). (Details in Supporting Information S1). The
121 drying method above yielded approximately 0.5g of sample per wastewater which was then
122 mixed with a measured quantity of paraffin wax which acts as a combustion aid to allow
123 complete combustion of the sample. Prior to the analysis wastewater samples, rigorous method
124 development of the drying and combustion methods was completed which showed the low
125 variability among replicas with this method (Supporting Information SI 1.4 and Table S2). A
126 strategic decision was made to complete the analysis of 107 independent repeat samples, rather
127 than a lower number of independent repeats but with replication (i.e. 36 triplicate samples).
128 Replicates are not an independent test of a hypothesis and do not therefore provide
129 reproducibility of the main result, they cannot be used to generate P values¹⁰. Previous research
130¹¹ used 38 triplicate samples and was not able to show a statistically significant correlation of
131 energy with wastewater parameters. The inherent heterogeneity of wastewater means that large
132 sample sizes are needed to draw statistically robust conclusions.

133

134 *2.4. COD and energy losses during drying*

135 To measure COD loss using centrifugal evaporation 40 mL of each wastewater sample was
136 dried simultaneously alongside the samples for the energy analysis, it was subjected to the same
137 drying times and forces. A lower volume (40ml rather than 400ml) was used as the dried sample
138 was very difficult to rehydrate into a homogenous solution. After drying, 40 mL of deionised water
139 was introduced to the drying flask which was then placed in a sonication bath for 10 minutes to

140 aid complete rehydration of the dried sample. COD was then measured on the sample using the
141 same standard procedure as for the original wastewater sample. Thus, percentage COD loss could
142 be calculated. Original COD (COD_{original}) and rehydrated COD ($COD_{\text{rehyd.}}$) was measured on 36
143 individual wastewater samples, with triplicate analysis of COD on both original wastewater
144 samples and rehydrated samples in all cases.

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146 2.5. Data analysis

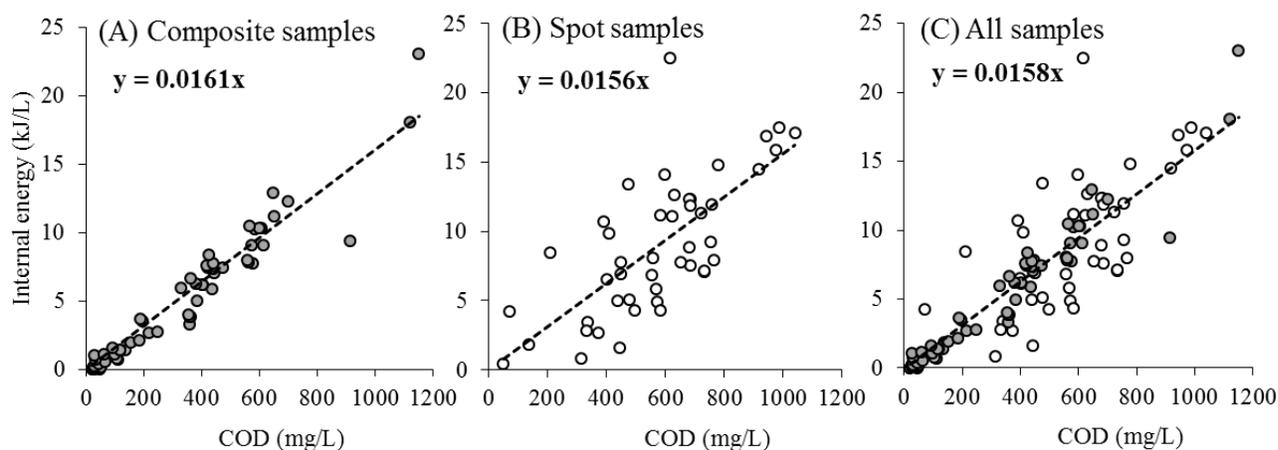
147 Summary statistics were computed in Excel 2013. Minitab 17 was used to calculate
148 Spearman's rank correlation coefficient (r_s) and significance levels (p) for these non-normally
149 distributed data.

150

151 3. Results and Discussion

152

153 There is a strong positive linear relationship between COD and energy content of municipal
154 wastewater (Figure 1). The correlation between COD and energy content is strongest for the
155 composite samples ($r_s = 0.967$, $p < 0.001$, $n = 62$; Figure 1A), and the regression line indicates an
156 energy value of 16.1 kJ/g COD. Calculating the regression equation for the spot samples gives
157 an energy content value of 15.6 kJ/g COD ($r_s = 0.855$, $p < 0.001$, $n = 48$; Figure 1B). Taking all
158 the data collected yields an energy value of 15.8 kJ/g COD ($r_s = 0.916$; $p < 0.001$, $n = 107$; Figure
159 1C). Wastewater is highly variable with changes in composition, strength and therefore energy
160 over any 24 hour period, creating greater scatter in the data points particularly at low COD values
161 (See Figure S1 in SI). Composite samples are collected and averaged over 24 hours, the value of
162 16.1 kJ/g COD using these samples is therefore more statistically robust.



163
 164 **Figure 1. The relationship between COD and energy content of municipal wastewater for**
 165 **(A) composite samples, (B) spot samples and (C) all samples. The line of best fit is put**
 166 **through the origin in all graphs on the basis that COD is used as an indicator of wastewater**
 167 **composition; zero COD therefore indicates zero energy, further graphs with an intercept**
 168 **are shown in S2 in SI.**

169
 170 The relationship between COD and energy content has been determined from analyses of
 171 municipal wastewaters of varying strength with respect to COD, but the four municipal
 172 wastewaters sampled are typical of COD concentrations of municipal wastewaters internationally
 173 430 mg/L to 800 mg/L for medium and high strength wastewaters respectively ¹². Summary
 174 statistics for the quality of the four wastewaters are shown in Table S2 (Supporting Information).
 175 Mean COD concentrations (\pm standard deviation) ranged from 378.9 ± 174.3 mg/L in Wastewater
 176 D to 684.8 ± 198.0 mg/L in Wastewater B, with an overall mean (all raw wastewaters) of $552.3 \pm$
 177 239.7 mg/L ($n = 72$). Primary treated effluent wastewater had mean COD concentrations ranging
 178 from 150.0 ± 55.9 mg/L to 450.0 ± 96.2 mg/L (overall mean of all wastewaters of 326.1 ± 147.0

179 mg/L ($n = 20$)), and mean secondary treated COD concentrations ranged from 24.9 ± 6.7 mg/L to
180 93.8 ± 27.4 mg/L (overall mean of all wastewaters of 45.8 ± 30.2 mg/L ($n = 24$)).

181 The large sampling effort of 107 wastewater samples was facilitated by the improved
182 drying method of centrifugal evaporation. This method of evaporation is used in chemical and
183 biochemical laboratories as a gentle yet efficient means of removing liquids or solvents from a
184 small sized samples. Larger capacity units, such as the one used in this study, are now also used in
185 the high end catering industry to produce highly reduced sauces. Results showed that the
186 centrifugal evaporation drying of samples has a greater COD recovery than both freeze-drying and
187 oven-drying (see Table 1). Using the centrifugal evaporation drying process there was no
188 particular difference in COD loss during drying of raw wastewater, primary treated and final
189 effluent, despite the large differences in initial COD: 87.4%, 82.6% and 82.9% respectively (see
190 Table 1). Losses of COD during drying have previously been ascribed to loss of volatile organic
191 compounds such as acetate⁸, and that may be the case with losses during centrifugal evaporation
192 drying also. Nevertheless, centrifugal evaporation incurs lower losses, and is also a quicker drying
193 process than freeze-drying taking approximately 3 days to dry up to 2.4 L of wastewater sample
194 as compared to 28 days to freeze dry 1.5 L⁸.

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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-drying¹³	2 ^B	647.3 ± 25.5	506.2 ± 24.4	77.8%
oven-drying¹³	2 ^B	647.3 ± 25.5	346.1 ± 15.2	53.7%

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

211 ^BData from Ref⁸; mean and standard deviations are calculated from triplicate analyses of two single
212 samples of wastewater

213

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

219

220 This may be because there are constituents of wastewater which may contribute to the
221 energy content but not the COD, most notably urea (enthalpy of combustion of -632 kJ/mol ¹⁵.
222 Scherson and Criddle ⁵ theoretically estimate the contribution of different compounds to the total
223 energy content of wastewater. They approximate nitrogen based compounds to account for 15%
224 of the total energy, COD based compounds accounting for the remaining 85%. The total energy

225 measured by bomb calorimetry is representative of the energy in the COD and the energy in the
 226 nitrogen based compounds (less the amount which has been volatilised during the drying process).
 227 If the COD is only 85% of this, then the true value of energy per gram of COD is 13.7 kJ/gCOD.
 228 This falls well within the range of known organic compounds shown in table 2. When TKN as a
 229 measure of nitrogen based compounds was added into the regression, there was an inconsequential
 230 improvement in the correlation producing an r^2 value of 93.2%, compared to r^2 of 92.9% with
 231 COD alone (details in SI ***). COD acts as a good proxy for both these measurements.

232

233 **Table 2 Common Organic Compounds and their Calculated Energy Values**

compounds ^a	type	formula	ΔH kJ/gCOD ^b
glutamic acid	proteins	C ₅ H ₉ NO ₄	13.4
aspartic acid		C ₄ H ₇ NO ₄	13.3
glucose	sugars	C ₆ H ₁₂ O ₆	14.6
xylose		C ₅ H ₁₀ O ₅	14.7
acetic acid	volatile fatty acids	CH ₃ COOH	13.6
butyric acid		CH ₃ CH ₂ CH ₂ COOH	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 ₆ H ₁₂ O ₆) _n	14.6
lignin		(C ₉ H ₁₀ O ₂) _n , (C ₁₀ H ₁₂ O ₃) _n or	14.1
		(C ₁₁ H ₁₄ O ₄) _n	

234 ^aA selection of different compound types selected, but all have been shown to be present at high
 235 concentration in municipal wastewater by Huang et al. ¹⁴.

236 ^b ΔH (kJ/gCOD) is calculated from deoxygenation enthalpy values presented by Sato ¹⁶, except for Fulvics
237 which is based on data in Reddy *et al.* ¹⁷. Values for energy content of additional organic compounds can
238 be found in Heidrich *et al.* ⁸.

239

240 Multiple regression analysis was used to determine the relationship between energy content
241 and all the wastewater parameters tested: COD, pCOD, TOC, DOC, VS, N-NH₄⁺ and P-PO₄³⁻ (see
242 Supporting Information S4 and S5). The parameters related directly to COD show a good
243 correlation with energy, N-NH₄⁺ and P-PO₄³⁻ are found to have no statistical correlation with
244 energy. The use of multiple variables within the regression analysis does not improve the model
245 beyond the use of COD alone. Within municipal wastewater COD can be regarded as a good proxy
246 for the concentration of all constituents. The value of 16.1 kJ/gCOD is therefore an empirical
247 mathematical factor of how much energy there is in wastewater per g of COD material it contains,
248 rather than the true relationship of how many kJ of energy is actually in each gram of COD.

249

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

256

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264 particular, assisted Ziyi Dai with site access and sample collection.

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268 **Supporting Information**

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

272

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