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Development of a method for calculating the entropy increase from organic oxidation in water environment through self-purification

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ABSTRACT

When a water body receives excess organic pollutants from external sources such as secondary effluent discharge, self-purification will occur and the water quality will be recovered to its background level. As the decomposition of organics will be accompanied by heat loss in the water body, it will result in an entropy increase (ΔS_C) according to the Second law of thermodynamics. In order to develop a method for the quantitative calculation of ΔS_C, the molar chemical exergy loss (Δb_x) was used as the surrogates of heat loss (ΔQ) under an assumption that the excess organic pollutants were decomposed by chemical oxidation. By using 201 organic substances of known molecular structures, a good proportional relation was found between Δb_x and the theoretical organic carbon contents (ThOC) with the proportional coefficients as $k_E = 52.576$ kJ g^{-1} ($R^2 = 0.9724$). Thus ΔS_C could be calculated according to the volume and the total organic carbon (TOC) concentration of the wastewater, and the background TOC concentration of the water body. The proposed method can provide a useful tool for assessing the environmental impact of organic pollutant discharge from the thermodynamic viewpoint.

Keywords: Impact assessment; Organic oxidation; Entropy increase; Chemical exergy

1. Introduction

Good-quality water is the basic requirement for the survival of human beings. Due to arid conditions, population growth, and increasing anthropogenic activities with rapid urbanization, the impact of wastewater effluent discharge on the aquatic ecological systems becomes an issue of wide concern [1]. Of various pollutants residual in the discharged effluent, the excess organic loading imposed on a receiving water body is one important aspect of surface water quality deterioration [2].

There are different ways to evaluate the water environment impact resulting from organic pollutant discharge. The most common way is to compare the water quality of the receiving water body with water quality criteria [3,4] or to analyze the variation of water quality resulting from organic discharge in the direction of flow which often requires a description of the relationship between the organic concentration (chemical oxygen demand (COD) or biological oxygen demand (BOD)) and dissolved oxygen [5]. The Streeter–Phelps equation has provided the theoretical

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foundation for the analysis [6]. The impacts of organic discharge on the downstream water quality can also be assessed by other elaborated models [7–9]. As water environment capacity (WEC) can measure the ability of an aquatic system to assimilate pollutant intrusion, WEC assessment has recently become a new approach [10], and is used for determining the degradation coefficient of organics in flowing water [11]. The WEC can also be quantified by Monte Carlo simulation combined with a water quality model [12].

The above-mentioned methods can be used either for studying the behavior of organic pollutants after entering a water body or for evaluating the water quality that is related to its suitability for water use. However, it is still difficult to obtain a parameter which can quantitatively evaluate the impact of organic discharge on the receiving water body. In a thermodynamic sense, water pollution can be viewed as water initially containing a low value of entropy being eventually turned to a high entropy value. As entropy can be used to determine the energy not available for work in a thermodynamic process, it may provide a measure of quality degradation in the referred system irrespective of any prescribed conditions such as the environmental standards. Therefore, the entropy increase can directly and quantitatively evaluate the impact of pollutant discharge [13]. Although, the thermodynamic entropy approach has already been applied in evaluation of water resources [14] and assessment of environmental sustainability [15], few studies have so far been conducted on assessing the impact of organic discharge on receiving water bodies following the Second Law of Thermodynamics.

According to the thermodynamic definition, the entropy increase (ΔS) in a reversible process is the amount of heat change (ΔQ) divided by the absolute temperature (T) at which the process takes place [16]. In a water body, if ΔQ is measurable then ΔS can be easily calculated. However, direct measurement or calculation of the heat change in water bodies is often difficult and alternative ways have to be discovered. For a chemical reaction under constant pressure, ΔS calculation can be conducted by using a surrogating parameter, namely exergy loss (ΔE_x) where exergy (E_x) is defined as the maximum amount of useful work produced when the system or the flow of matter comes to equilibrium with the reference environment [17], while ΔE_x refers to the exergy reduction caused by the irreversibility of actual process when the condition of the system or the matter was changed [18]. The exergy approach has been used in a number of studies for the analysis of energy consumption in wastewater treatment plants [19], establishment of an aquatic ecosystem model [20], assessment of environmental costs of water resources [18,21], water quality evaluation [22,23], minimization of energy consumption [24], and optimization of process systems [25]. In addition, thermodynamic optimization has been successfully developed for metabolic systems. The heuristic idea of introducing thermodynamic analysis into metabolic engineering presents a new way to rationalize metabolic pathway analysis, hence providing a better control mechanism for industrial bioprocesses [26,27]. However, there is a lack of studies calcuating the ΔE_x in aquatic systems due to the intrusion of organic pollutants.

In natural waters, the most common route of organic decomposition is the oxidative conversion of the organic matter into carbon dioxide, water and other simple inorganic forms. For an organic substance of known molecular structure, its ΔE_x can be calculated according to its oxidation reaction. However, it is difficult to calculate ΔE_x of organic substances without known molecular structure. In fact, organic substances in a water media such as the secondary effluent are heterogeneous organic mixtures that have not known each molecular structure, their gross amount can only be characterized by comprehensive indices such as COD, BOD, and total organic carbon (TOC). Thus, the aim of this study is to find a way for calculating ΔE_x based on the gross amount of organic substances, and then to establish a method for quantitatively evaluating the entropy increase in water bodies due to receiving organic pollutant discharge.

2. Material and methods

2.1. Calculation of molar exergy loss for organic substances

The exergy (E_x) of a chemical compound is the amount of energy released during the chemical reaction for its formation at equilibrium with the reference environment. It consists of two parts, namely the physical exergy and the chemical exergy [28]. The physical exergy (E_{ph}) is the obtainable energy due to the differences in temperature and pressure between the reaction system and the surrounding environment, while the chemical exergy (E_{ch}) is the obtainable energy due to the disequilibrium of the chemical composition of the reaction system with the surrounding environment at constant temperature and pressure. For the oxidative decomposition of organic substances in the water environment, the variation of temperature and pressure in the decomposition process is trivial so that the physical exergy can be neglected and only the chemical exergy needs to be calculated [19,21].

The chemical exergy of a substance also consists of two parts, i.e. the reactional exergy resulting from the chemical reactions necessary to produce species that can exist as stable components in the environment, and the concentrational exergy resulting from the necessary processes to match the chemical concentration of the produced species to their chemical concentrations in the environment [29]. Setting appropriate reference environment (RE) is a prerequisite for exergy calculation. By definition, the exergy of the RE should be zero, so that each component in the RE has to be in a dynamic equilibrium and chemical reaction cannot occur between the component substances. In this study, if the natural water environment is considered as the RE, the reference temperature and pressure are set as 298.15 K and 101.3 kPa, respectively, and the reference substances include CO_2, H_2O (l), N_2, and SO_2 [30].

Regarding an organic substance i in the reaction system, its standard molar chemical exergy (b_x) can be calculated as [31]:

$$b_x = b_{x1} + b_{x2} = \left(\Delta_f G^0 + \sum_e n_e b_{ch,n_e}\right) + RT_0 \cdot \ln \frac{C_i}{C_{i,0}} \tag{1}$$

where b_{x1} is the molar reactional exergy (kJ mol^{-1}), $b_{x1} = \Delta_f G^0 + \sum n_e b_{ch,n_e}$; $\Delta_f G^0$ is the standard Gibbs free energy of formation (kJ mol^{-1}); n_e is the molar number of element e forming the substance i; b_{ch,n_e} is the corresponding specific chemical exergy (kJ mol^{-1}); b_{x2} is the molar concentrational exergy of substance i (kJ mol^{-1}), $b_{x2} = RT_0 \ln \frac{C_i}{C_{i,0}}$; C_i is the concentration of substance i in the system (g m^{-3}); $C_{i,0}$ is the background concentration of substance i in the RE (g m^{-3}); R is the gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1}); and T_0 is the standard temperature of the environment (298.15 K).

The molar reactional exergy b_{x1} for an organic substance of known molecular structure is calculated from its $\Delta_f G^0$, the corresponding specific chemical exergy of each component element b_{ch,n_e} and its molar number n_e. Taking vinyl sulfoxide (C_4H_6OS) as an example, its standard Gibbs free energy is known as $\Delta_f G^0(C_4H_6OS) = -59.23$ kJ mol^{-1} [16], and the specific chemical exergy of each component element can be obtained as $b_{ch,C} = 410.53$ kJ mol^{-1}, $b_{ch,H} = 117.61$ kJ mol^{-1}, $b_{ch,O} = 1.966$ kJ mol^{-1} and $b_{ch,S} = 602.79$ kJ mol^{-1} [32]. Based on the first term on the right side of the Eq. (1), its b_{x1} can be calculated as:

$$\begin{aligned} b_{x1}(C_4H_6OS) &= -59.23 + 4 \times 410.53 + 6 \times 117.61 \\ &\quad + 1.966 + 602.7 \\ &= 2893.31 \ (\text{kJ mol}^{-1}) \end{aligned} \tag{2}$$

Regarding the molar concentrational exergy b_{x2}, it can be calculated from the organic concentration C_i and its corresponding background concentration $C_{i,0}$ (the second term on the right side of Eq. (1)).

The molar chemical exergy loss (Δb_x) is the difference between the chemical exergy before and that after the reaction, it can be calculated as:

$$\begin{aligned} \Delta b_x &= \Delta b_{x1} + \Delta b_{x2} \\ &= \left(\sum \upsilon_{\text{react}} b_{x1}(\text{react}) - \upsilon_{\text{prod}} \cdot b_{x1}(\text{prod})\right) \\ &\quad + RT \ln \frac{C_i}{C_{i,0}} \end{aligned} \tag{3}$$

where Δb_{x1} is the loss of molar reactional exergy after the reaction (kJ mol^{-1}); Δb_{x2} is the loss of molar concentrational exergy after the reaction (kJ mol^{-1}); υ_{react} and υ_{prod} are the stoichiometric coefficient of the product and that of the reactant, respectively; b_{x1}(react) and b_{x1}(prod) are the specific chemical exergy of the product and that of the reactant, respectively (kJ mol^{-1}). The final term on the right side of Eq. (3) is the molar concentrational exergy before the reaction because it is supposed that after the reaction the organic concentration C_i is reduced to the background concentration $C_{i,0}$ so that the molar concentrational exergy after the reaction becomes zero.

2.2. *Entropy calculation based on exergy loss*

The introduction of entropy in classical thermodynamics is related to equilibrium state and reversible transformation. An isolated system is considered to be reversible if $\Delta S = 0$, or irreversible if $\Delta S > 0$. When an irreversible system is considered, mathematical inequalities appear, so, entropy generation was introduced just to avoid them. Consequently, the second law defines the entropy variation, ΔS, for an irreversible system, as [17]:

$$\Delta S = \int \left(\frac{\delta Q}{T}\right)_{\text{rev}} = \Delta S_e + S_g \tag{4}$$

where ΔS_e is the reversible entropy variation (J K^{-1}) and S_g is the entropy generation (J K^{-1}), i.e. the entropy variation due to irreversibility.

An aquatic system and its surrounding create an isolated composite system where the reversible entropy variation is zero, thus ΔS is equal to S_g. As discussed above, exergy is a measure of the potential of the system to cause changes, as a consequence of not being completely in stable equilibrium relative to the reference environment. Moreover, the

GouyStodola theorem allows us to evaluate the irreversibility and the dissipations in the interaction between systems and their environment, by considering entropy generation, which is related to the exergy lost by the systems during the interactions themselves. Therefore, according to the Gouy–Stodola's law [33], the exergy loss of the reaction equals the product of the entropy increase (ΔS) and the environmental temperature:

$$\Delta E_x = T_0(S_0 - S) = T_0 \Delta S \tag{5}$$

where ΔE_x is exergy loss of the reaction (kJ), T_0 is the absolute temperature under the standard condition (298.15 K), S_0 is the entropy of the environment, and S is the entropy of the system at thermodynamic equilibrium.

Eq. (5) can be rewritten as:

$$\Delta S = \frac{\Delta E_x}{T_0} \tag{6}$$

2.3. Organics and their degradation by chemical oxidation

Organic substances commonly existing in natural water and the secondary effluent may include pure hydrocarbons (saturated alkane, unsaturated alkane, aromatic hydrocarbons, etc.) and organic compounds containing additional elements such as oxygen, nitrogen, sulfur, etc. In order to investigate the thermodynamic properties of different organic substances, 201 organic chemicals of known molecular structure and with available thermodynamic information related to their oxidation reactions were selected for this study. They can be classified into 9 categories according to their molecular structure as shown in Table 1.

Considering a condition that each of the organic substances listed in Table 1 is completely decomposed into the simplest forms of inorganic substances by chemical oxidation, a series of chemical reaction equations could be proposed for their decomposition. The reference substances of CO_2, H_2O (l), N_2, and SO_2, which are required for the exergy analysis, were supposed to be the final products of oxidation reactions. If a general molecular formula $C_xH_yO_zN_tS_m$ was used to represent all the organic substances listed in Table 1, then the oxidation reactions could be written in a general equation as:

$$\begin{aligned} &C_xH_yO_zN_tS_m + (x + y/4 + m - z/2)O_2 \\ &\quad \rightarrow xCO_2 + y/2H_2O + t/2N_2 + mSO_2 \end{aligned} \tag{7}$$

From Eq. (7), the content of the theoretical organic carbon (ThOC), which is usually an important parameter for measuring the quantity of the organic substances, could be obtained as:

$$\text{ThOC} = 12x \tag{8}$$

where the value of 12 is the molecular mass of carbon element (g mol^{-1}), and x is the number of carbon elements contained by the organic compound, so that the unit of ThOC is also g mol^{-1}.

3. Results

3.1. Relation between Δb_{x1} and ThOC for known organic substances

As discussed in Section 2.1, the chemical exergy loss (Δb_x) of an organic substance consists of Δb_{x1}, the molar reactional energy loss, and Δb_{x2}, the molar concentrational exergy loss. Of them, the calculation of Δb_{x1} should use the thermodynamic database for the molar reactional exergy of the related organic substances and the reference substances, and the stoichiometic coefficients for the reactants and products in the oxidation reaction shown in Eq. (7). Taking vinyl

Table 1
Organic substances used for Δb_{x1} and ThOC calculation

Category	Formula	Number of constituting elements	Number of substances
Acyclic alkane	C_xH_y	x = 1–20, y = 2x + 2	20
Cycloalkane and alkene	C_xH_y	x = 2–10, y = 2x	18
Alkyne and diene	C_xH_y	x = 2–10, y = 2x − 2	14
Aromatic hydrocarbons	C_xH_y	x = 6–16, y = 6–26	8
Organic compounds containing oxygen	$C_xH_yO_z$	x = 1–10, y = 2–18, z = 1–2	79
Organic compounds containing nitrogen	$C_xH_yO_zN_t$	x = 1–9, y = 3–19, t = 1–2, z = 0–4	33
Organic compounds containing sulfur	$C_xH_yO_zS_m$	x = 1–8, y = 4–18, m = 1–2, z = 0–1	29

sulfoxide (C_4H_6OS) for instance again, its oxidation reaction is:

$$C_4H_6OS + 6O_2 \rightarrow 4CO_2 + 3H_2O + SO_2 \tag{9}$$

Standard molar reactional exergy of vinyl sulfoxide has already been obtained from Eq. (2) as $b_{x1}(C_4H_6OS)$ = 2,893.31 kJ mol^{-1}, while the b_{x1} values for the reference substances O_2, CO_2, H_2O, and SO_2 are 3.93, 20.13, 0.9, and 306.52 kJ mol^{-1}, respectively [32]. Substituting these data and the stoichiometric coefficient of each substance into Eq. (3), the standard molar reactional exergy loss for the oxidation of C_4H_6OS was calculated as:

$$\begin{aligned}\Delta b_{x1}(C_4H_6OS) &= \sum v_{\text{react}} b_{x1}(\text{react}) - \sum v_{\text{prod}} b_{x1}(\text{prod}) \\ &= 2893.31 + 6 \times 3.93 - 4 \times 20.13 - 3 \\ &\quad \times 0.9 - 306.52 \\ &= 2527.15\ (\text{kJ mol}^{-1})\end{aligned} \tag{10}$$

The value of ThOC for C_4H_6OS was calculated from Eq. (8) as:

$$\text{ThOC}(C_4H_6OS) = 12 \times 4 = 48\ (\text{g mol}^{-1}) \tag{11}$$

Similar calculations were conducted for obtaining the values of Δb_{x1} and ThOC for each of the 201 organic substances listed in Table 1. By plotting all these data with ThOC as the abscissa and Δb_{x1} as the ordinate, Fig. 1 was obtained to show a general tendency of increase in the Δb_{x1} values with the ThOC value. By correlative calculation, a linear proportional relation was obtained as:

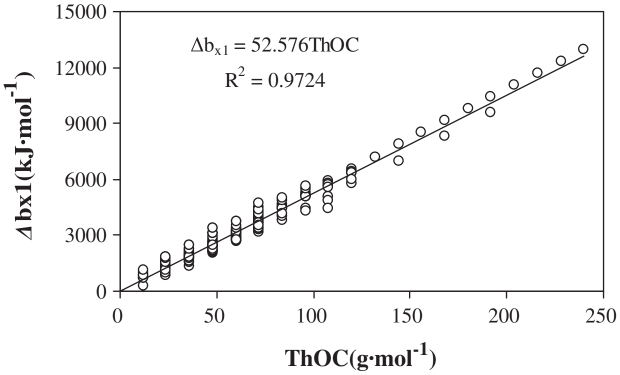

Fig. 1. Relation between Δb_{x1} and ThOC for known organic substances.

$$\Delta b_{x1} = k_E\ \text{ThOC} \quad (R^2 = 0.9724) \tag{12}$$

where ThOC and Δb_{x1} are g mol^{-1} and kJ mol^{-1}, so that the dimension of the proportional coefficient k_E = 52.576 should be kJ g^{-1}.

3.2. Method of ΔS_C calculation for impact assessment of organic pollution due to secondary effluent discharge

As discussed in Section 2.1, in the case of organic oxidation in water environment the physical exergy can be ignored so that the exergy loss ΔE_x is mainly contributed by the chemical exergy loss of the organic substance ΔE_{ch}, which equals the product of the molar chemical exergy loss Δb_x and the molar number n of the organic substance. Therefore, the entropy increase for organic decomposition (ΔS_C) can be calculated as:

$$\Delta S_C = \frac{\Delta E_{ch}}{T_0} = \frac{n\ \Delta b_x}{T_0} = \frac{n}{T_0}(\Delta b_{x1} + \Delta b_{x2}) = \Delta S_{C1} + \Delta S_{C2} \tag{13}$$

where $\Delta S_{C1} = \frac{n}{T_0}\Delta b_{x1}$ and $\Delta S_{C2} = \frac{n}{T_0}\Delta b_{x2}$ are the entropy increase for organic decomposition due to Δb_{x1} and Δb_{x2}, respectively.

Based on our previous study [34], TOC concentration of the secondary effluent can be used to replace the ThOC. Under the condition of the discharging organics were totally decomposed in the water body, Eq. (12) can be obtained for calculating Δb_{x1} directly from TOC. Therefore, ΔS_{C1} can be expressed as:

$$\Delta S_{C1} = \frac{k_E \cdot \text{TOC} \cdot V}{T_0} \tag{14}$$

where k_E = 52.576 kJ g^{-1}, TOC is the TOC concentration of the effluent (g m^{-3}), and V is the volume of the secondary effluent discharge (m^3).

However, it should be considered that through self-purification the organic concentration can only be reduced to the background level (TOC_0), so that the practical reduction of the organic concentration should be:

$$\Delta\text{TOC} = \text{TOC} - \text{TOC}_0 \tag{15}$$

Using ΔTOC to replace TOC in Eq. (14), the equation of entropy increase for organic decomposition due to Δb_{x1} can be obtained as:

$$\Delta S_{C1} = \frac{k_E \cdot \Delta \mathrm{TOC} \cdot V}{T_0} \tag{16}$$

Regarding ΔS_{C2}, as the concentrational exergy loss, Δb_{x2} is only related to the concentration ratio of the organic substances before and after the reaction, and the molar number of the organic carbon degraded by the reaction can be evaluated as $n = \frac{\Delta \mathrm{TOC} \cdot V}{12}$, where 12 is the unit mass of carbon element (g mol^{-1}), it can be calculated as:

$$\Delta S_{C2} = \frac{n \cdot \Delta b_{x2}}{T_0} = \frac{\Delta \mathrm{TOC} \cdot V \cdot R}{12} \ln \frac{\mathrm{TOC}}{\mathrm{TOC}_0} \tag{17}$$

Comparing Eqs. (17) and (16), the ratio of ΔS_{C2} to ΔS_{C1} is:

$$\frac{\Delta S_{C2}}{\Delta S_{C1}} = \frac{R \cdot T_0}{12 k_E} \ln \frac{\mathrm{TOC}}{\mathrm{TOC}_0} = 0.003929 \ln \frac{\mathrm{TOC}}{\mathrm{TOC}_0} \tag{18}$$

where $R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}, $T_0 = 298.15$ K, and $k_E = 52.576$ kJ g^{-1} are used for the calculation.

Table 2 shows the relation between $\mathrm{TOC}/\mathrm{TOC}_0$ and $\Delta S_{C2}/\Delta S_{C1}$. It can be seen that although $\Delta S_{C2}/\Delta S_{C1}$ increases with $\mathrm{TOC}/\mathrm{TOC}_0$, even when the organic carbon concentration in the discharged effluent (TOC) is as high as 1,000 times of the background concentration (TOC_0), the value of ΔS_{C2} is only 3.6% of the ΔS_{C1}, indicating a very small effect of the diffusion due to concentrational difference on entropy increase in water environment. In the case of secondary effluent discharge, the concentration ratio is usually much lower, and the contribution of ΔS_{C2} will be negligibly small. Therefore, ΔS_C can be calculated as:

$$\Delta S_C = \Delta S_{C1} = \frac{k_E \cdot \Delta \mathrm{TOC} \cdot V}{T_0} \tag{19}$$

In the thermodynamic equilibrium, the ΔS values can be calculated using the van't Hoff equation. In this case, if the oxidation reaction of vinyl sulfoxide is reversible, the ΔS value of 1 mol of C_4H_6OS was calculated as 0.578 kJ K^{-1} under temperature of $T_0 = 298.15$ K. However, by using the proposed exergy approach, ΔS value of 1 mol of C_4H_6OS, for an irreversible process was calculated as 8.46 kJ K^{-1} under the same temperature. It can be seen that the ΔS value of the irreversible process is larger than the reversible process. Accordingly, Eq. (19) is suitable for calculating the entropy increase of organic decomposition in the irreversible system or process.

Table 2
Relation between $\mathrm{TOC}/\mathrm{TOC}_0$ and $\Delta S_{C2}/\Delta S_{C1}$

$\frac{\mathrm{TOC}}{\mathrm{TOC}_0}$	1	10	100	1,000	10,000
$\frac{\Delta S_{C2}}{\Delta S_{C1}}$	0	0.009	0.018	0.027	0.036

4. Discussion

4.1. Influence of the molecular structure of the organic substances on their Δb_x

Although a good linear relationship was found between the theoretical organic carbon content ThOC and Δb_{x1} (Fig. 1) for all the organic substances of known molecular structures were investigated in this study, the organic substances with the same ThOC, i.e. the same number of carbon elements in their molecules, do not show exactly the same values of Δb_{x1}. The molecular structures and/or the constituent elements contained in the organic substances are important factors to influence their chemical oxidation processes, and eventually the calculated values of Δb_{x1}. The organic substances used for thermodynamic discussion in this study can be roughly classified into 4 types, namely pure hydrocarbons with only C and H, compounds with C, H, and O, compounds with C, H, O, and S or N, and compounds with C, H, and S or N. Taking the organic substances with 2, 3, and 4 carbon elements for a detailed comparison, Fig. 2 is obtained to show the influence of the organic type on the calculated Δb_{x1} values.

The average Δb_{x1} values for the organic substances with 2, 3, and 4 carbon elements are calculated as 1,408.7, 1,921.8, and 2,572.2 kJ mol^{-1}, respectively (the dotted lines in Fig. 2), showing the tendency of increasing Δb_{x1} with ThOC as discussed in Section 3.1. Generally speaking, regardless of the number of carbon elements the Δb_{x1} values of each organic molecular type are located in similar area referring to the average Δb_{x1} value line. For the organic compounds with C and H, their Δb_{x1} values do not scatter widely and are relatively close to the average values, while for the organic compounds with C, H, and O, their Δb_x values scatter widely and are located in the area under the average Δb_{x1} value line. In the case of the organic compounds with C, H, O, and S or N, their Δb_x values vary in a still wide range surrounding the average Δb_{x1} value line. Comparing with the aforementioned three types, the organic compounds with C, H, and S or N show the highest Δb_x values which are scattered in the area above the average Δb_{x1} value line.

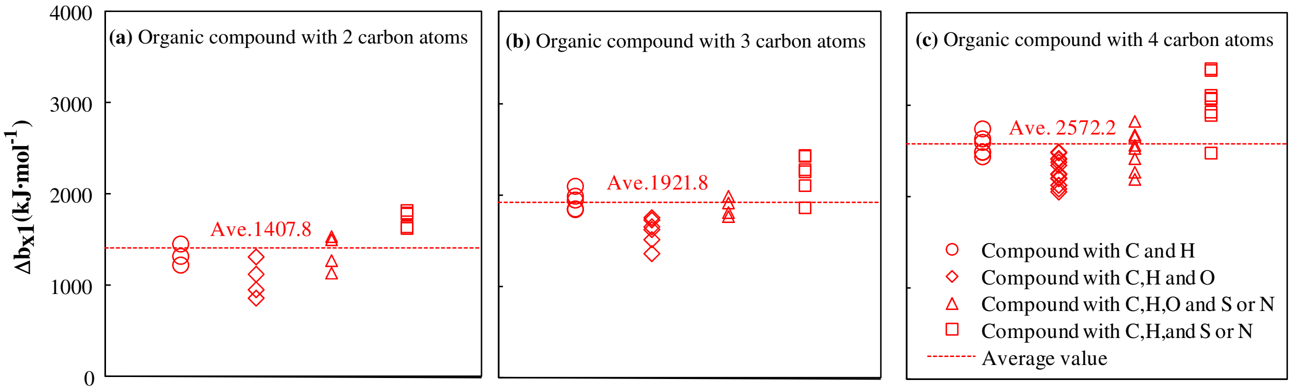

Fig. 2. Characteristic distribution of the Δb_{x1} values for substances with 2, 3, and 4 carbon atoms in their organic molecules.

The above-mentioned characteristic distribution of the Δb_{x1} values for the organic substances of different types is principally related to the energy consumed in the chemical oxidation process for the breakdown of the organic molecules and the formation of the oxidation products. For the carbon element originally contained in the organic molecules, its final form in the oxidation product is CO_2. If there are oxygen atoms combined with the carbon atoms in the organic molecules, it may not be necessary for the original C–O binding to be completely broken down firstly and then to form the CO_2 as the oxidation product. Therefore, comparing with the pure hydrocarbons that contain only C and H, the hydrocarbons with additional oxygen might need less energy in their oxidation process though their carbon contents are the same. Such an assumption may explain the reason for the lower Δb_{x1} values of the organic compounds with C, H, and O than that of the organic compounds with only C and H as shown in Fig. 2. As for the organic compounds with C, H, and S or N, their higher Δb_{x1} values may be explained as the consumption of additional energy for forming SO_2 or N_2 as the final products, while for the organic compounds with C, H, O, and S or N, the existence of oxygen in the organic molecules may also be the reason for the lower Δb_{x1} values than that in the former case.

Organic substances being discharged into the water environment are heterogeneous and diverse. As the method proposed in this study is to calculate the entropy increase ΔS_C directly from the TOC concentration, its essence is to use the average Δb_x to characterize the energy consumption for the oxidization of organic substances with the same carbon contents. This method inevitably has its theoretical limitation for ignoring the influence of the organic composition and molecular structure on the ΔS_C calculation. However, as shown in Figs. 1 and 2, the general tendency of the linear increase in Δb_{x1} with the organic carbon content is apparent. Using their average values to estimate the entropy increase can be considered statistically significant and reasonable.

4.2. *Limitation and reasonability of taking chemical oxidation as the sole process of organic decomposition*

In a natural water body, the reduction of excess organic substances by self-purification may depend on chemical oxidation and also other processes such as physical adsorption by suspended particles and biodegradation under the action of micro-organisms [35]. The method for ΔS_C calculation developed in this study is under the assumption that chemical oxidation is the sole process of organic decomposition. This is also a theoretical limitation of this method for ignoring the effects of other processes to contribute to organic removal. However, in the case of effluent discharge from domestic wastewater treatment plants, because the secondary effluent has undergone a biological process where most of the biodegradable organic substances may have already been removed, and the secondary sedimentation process where most of the hydrophobic organic substances may have already been trapped by high concentration sludge particles, the residual organic matter in the secondary effluent may be mostly non-biodegradable, hydrophilic, and of low molecular weight [36,37]. For such kind of organic substances, it is reasonable to take the chemical oxidation as the sole process for the final degradation of the access organic substances in the receiving water body.

4.3. Differences between the enthalpy and exergy approaches for ΔS_C calculations

In the authors' previous study [34], ΔS_C calculation was obtained by analyzing the standard molar enthalpy change ($\Delta_r H^0$). Although both the $\Delta_r H^0$ and Δb_x analyses have followed the Second Law of Thermodynamics, and then, the two approaches have resulted in almost identical equations for ΔS_C calculation based on the quantity of TOC reduced by the reaction, there are differences between $\Delta_r H^0$ and Δb_x analyses. Firstly, the reference environment for $\Delta_r H^0$ analysis and that for Δb_x analysis are not the same. For $\Delta_r H^0$ analysis, the standard condition of temperature at 298 K and pressure at 101.3 kPa has to be referred, under which the standard molar enthalpy of formation for any stable element is set as zero, while for Δb_x analysis, the reference environment is a natural water without existence of foreign substances other than the reference substances of CO_2, H_2O (l), N_2, and SO_2. Secondly, the range of processes involved for $\Delta_r H^0$ analysis and that for Δb_x analysis are not the same. The $\Delta_r H^0$ analysis only focuses on the process of organic decomposition by chemical oxidation, while the Δb_x analysis needs considerations not only on the chemical reaction, but also the diffusion of organic substances in the reaction system. However, as discussed in Section 3.2, the effect of the diffusion due to concentrational differences is negligibly small on the ΔS_C calculation.

4.4. Application of ΔS_C calculation

Upgrading of WWTP may be necessary to meet the existing effluent quality and/or to meet the stricter future effluent quality. According to Chinese standard for pollutant discharge [38], there are basically two classes of effluent quality applicable to urban domestic wastewater treatment plants: one is Class I-B suitable for the existing WWTPs with effluent discharging to unprotected surface waters, and another is Class I-A for the newly built or upgraded WWTPs with effluent discharging to protect surface waters. As water contamination is a serious problem for many surface waters in China, nowadays most municipalities are strengthening regulations on effluent discharge from WWTPs. Meeting with Class I-A is becoming the mainstream of effluent quality control. In order to evaluate the effect of WWTP upgrading, the effluent quality with Class I-B (COD = 60 mg L^{-1}) for existing WWTP and the effluent quality with Class I-A (COD = 50 mg L^{-1}) for upgraded WWTP were considered. For the receiving water body, if the quality is conforming with Grade III standard [39] which is the minimum requirement for surface water usable as source water for domestic water supply, its background COD concentration can be set to 20 mg L^{-1}. Considering the ratio of TOC/COD as 2.7:7.1 [34] and using Eq. (19) to calculate the ΔS_C after unit quantity (e.g. 1,000 m^3) of the effluent is discharged into the water body, the ΔS_C values are obtained as 2,682.4 and 2,011.8 kJ K^{-1} for the discharges from an existing WWTP and an upgraded WWTP, respectively, at an average water temperature of $T_0 = 298.15$ K. This implies a 25% ΔS_C reduction after the WWTP upgrading.

From a thermodynamic viewpoint, the reduction of ΔS_C implies less energy dissipation in the form of waste heat which results in less negative impacts on the environment. In this way, the water pollution factor is converted to a factor that directly and quantitatively measures the environmental impact. This is the advantage of the entropy approach over other methods for assessing the impact of organic discharge from the secondary effluent on the water environment. The proposal of Eq. (19) for calculating ΔS_C from the excess organic quantity ΔTOC is based on the assumption that chemical oxidation is the sole process for organic decomposition under a condition that the organic loading is not beyond the capacity of the receiving water for self-purification. Other possible actions in the water for organic decomposition or removal, such as biological degradation, adsorption and sedimentation, etc., are ignored in this paper. Therefore, further studies are still needed to broaden the suitability of the ΔS_C calculation in various cases.

5. Conclusions

Based on the Second Law of Thermodynamics, the impact of organic discharge, such as the secondary effluent from domestic wastewater treatment plants, on the receiving water body was analyzed using the entropy increase ΔS_C resulting from organic decomposition as a comprehensive thermodynamic index. Under the assumption that the excess organic pollutants entering the water body were decomposed by chemical oxidation to bring about a recovery of the water quality to its background level, the method of ΔS_C calculation was developed through quantitative evaluation of the chemical exergy loss Δb_x in the oxidation process. By computing 201 organic substances of varied molecular structures, a good linear relationship was found between the calculated Δb_x values and the organic carbon content TOC. This led to the proposal of the equations for calculating ΔS_C directly from the volume and TOC concentration of the wastewater, and the background TOC concentration of the receiving water body. Although the method proposed still has its theoretical limitation such as ignoring the influence of organic composition and molecular structures of the organic substances, and the possible actions other than chemical oxidation that may also contribute to the self-purification of the excess organic pollutants, it provides a way for a general evaluation of the entropy increase from the total quantity of the excess organic matter entering the water environment. Further studies are still needed to broaden the suitability of the proposed method in various cases.

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Symbols

b_{ch,n_e} — specific chemical exergy (kJ mol^{-1})
b_x — standard molar chemical exergy (kJ mol^{-1})
b_{x1} — molar reactional exergy (kJ mol^{-1})
b_{x2} — molar concentrational exergy of substance, i (kJ mol^{-1})
C_i — concentration of substance i in the system (g m^{-3})
$C_{i,0}$ — background concentration of substance i in the RE (g m^{-3})
n_e — molar number of element e forming the substance i
n — molar number of the organic substance (mol)
R — gas constant, 8.314 × 10^{-3} kJ K^{-1} mol^{-1}
S_0 — entropy of the environment (J K^{-1})
S_g — entropy generation (J K^{-1})
S — entropy of the system at thermodynamic equilibrium (J K^{-1})
ThOC — content of the theoretical organic carbon (g mol^{-1})
T_0 — standard temperature of the environment (K)
TOC — total organic carbon concentration of the effluent (g m^{-3})
TOC$_0$ — total organic carbon concentration of the background level (g m^{-3})
V — volume of the secondary effluent discharge (m^3)
v_{react} — stoichiometric coefficient of the reactant
v_{prod} — stoichiometric coefficient of the product
x — number of carbon elements contained by the organic compound
Δb_{x1} — loss of molar reactional exergy after the reaction (kJ mol^{-1})
Δb_{x2} — loss of molar concentrational exergy after the reaction (kJ mol^{-1})
ΔE_x — exergy loss of the reaction (kJ)
$\Delta_f G^0$ — standard Gibbs free energy of formation (kJ mol^{-1})
ΔS — entropy increase (J K^{-1})
ΔS_e — reversible entropy variation (J K^{-1})

References

[1] K.N. Kalscheur, R.R. Penskar, A.D. Daley, S.M. Pechauer, J.J. Kelly, C.G. Peterson, K.A. Gray, Effects of anthropogenic inputs on the organic quality of urbanized streams, Water Res. 46 (2012) 2512–2524.

[2] N. Hudson, A. Baker, D. Reynolds, Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—A review, River Res. Appl. 23 (2007) 631–649.

[3] B.N. Lohani, J.W. Evans, R.R. Everitt, H. Ludwig, R.A. Carpenter, S.-L. Tu, Environmental Impact Assessment for Developing Countries in Asia, Asian Development Bank, Manila, 1997.

[4] D. Vollmer, Urban waterfront rehabilitation: Can it contribute to environmental improvements in the developing world? Environ. Res. Lett. 4 (2009) 237–266.

[5] M.J. Gómez, S. Herrera, D. Solé, E. García-Calvo, A.R. Fernández-Alba, Spatio-temporal evaluation of organic contaminants and their transformation products along a river basin affected by urban, agricultural and industrial pollution, Sci. Total Environ. 420 (2012) 134–145.

[6] G. Mannina, G. Viviani, Water quality modelling for ephemeral rivers: Model development and parameter assessment, J. Hydrol. 393 (2010) 186–196.

[7] E. Llorens, F. Thiery, S. Grieu, M. Polit, Evaluation of WWTP discharges into a Mediterranean river using KSOM neural networks and mass balance modelling, Chem. Eng. J. 142 (2008) 135–146.

[8] B.Y. Chen, S.N. Nam, P.K. Westerhoff, S.W. Krasner, G. Amy, Fate of effluent organic matter and DBP precursors in an effluent-dominated river: A case study of wastewater impact on downstream water quality, Water Res. 43 (2009) 1755–1765.

[9] R.B. Zhang, X. Qian, H.M. Li, X.C. Yuan, R. Ye, Selection of optimal river water quality improvement programs using QUAL2K: A case study of Taihu Lake Basin, China, Sci. Total Environ. 431 (2012) 278–285.

[10] M. Han, J.B. Mu, F.L. Sun, L. Cheng, Z. Hao, Estimation of water environment capacity: Example as four basins in Shangdong Province, China, Proc. Environ. Sci. 2 (2010) 1919–1926.

[11] Y.X. Li, R.Z. Qiu, Z.F. Yang, C.H. Li, J.S. Yu, Parameter determination to calculate water environmental capacity in Zhangweinan Canal Sub-basin in China, J. Environ. Sci. 22 (2010) 904–907.

[12] R.M. Liu, C.C. Sun, Z.X. Han, L. Chen, Q. Huang, Y.X. Chen, S.H. Gao, Z.Y. Shen, Water environmental capacity calculation based on uncertainty analysis: A case study in the Baixi watershed area, China, Proc. Environ. Sci. 13 (2012) 1728–1738.

[13] S. Tai, T. Goda, Entropy analysis of water and wastewater treatment processes, Int. J. Environ. Stud. 25 (1985) 13–21.

[14] V.P. Singh, The entropy theory as a tool for modelling and decision-making in environmental and water resources, Water SA 26 (2000) 1–12.

[15] M. Teles dos Santos, S.W. Park, Sustainability and biophysics basis of technical and economic processes: A survey of the reconciliation by thermodynamics, Renew. Sustain. Energy Rev. 23 (2013) 261–271.

[16] V. Čápek, D.P. Sheehan, Challenges to the Second Law of Thermodynamics, Springer, New York, NY, 2005.

[17] U. Lucia, Entropy and exergy in irreversible renewable energy systems, Renew. Sustain. Energy Rev. 20 (2013) 559–564.

[18] A. Valero, J. Uche, A. Valero, A. Martínez, J. Escriu, Physical hydronomics: Application of the exergy analysis to the assessment of environmental costs of water bodies. The case of the Inland Basins of Catalonia, Energy 34 (2009) 2101–2107.

[19] D. Hellström, An exergy analysis for a wastewater treatment plant—An estimation of the consumption of physical resources, Water Environ. Res. 69 (1997) 44–51.

[20] S. Mandal, S. Ray, S.E. Jørgensen, Exergy as an indicator: Observations of an aquatic ecosystem model, Ecol. Inform. 12 (2012) 1–9.

[21] A. Martínez, J. Uche, A. Valero, A. Valero-Delgado, Environmental costs of a river watershed within the European water framework directive: Results from physical hydronomics, Energy 35 (2010) 1008–1016.

[22] G.Q. Chen, X. Ji, Chemical exergy based evaluation of water quality, Ecol. Model. 200 (2007) 259–268.

[23] L.Q. Huang, G.Q. Chen, Y. Zhang, B. Chen, S.J. Luan, Exergy as a unified measure of water quality, Commun. Nonlinear Sci. Numer. Simul. 12 (2007) 663–672.

[24] Y. Wang, S. Wu, X. Feng, C. Deng, An exergy-based approach for hydrogen network integration, Energy 86 (2015) 514–524.

[25] F. Xiao, G. Zhong, Z. Ping, Z. Gu, Cumulative exergy analysis of heat exchanger production and heat exchange processes, Energy Fuel 18 (2004) 1194–1198.

[26] M. Xu, S. Bhat, R. Smith, G. Stephens, J. Sadhukhan, Multi-objective optimisation of metabolic productivity and thermodynamic performance, Comput. Chem. Eng. 33 (2009) 1438–1450.

[27] M. Xu, R. Smith, J. Sadhukhan, Optimization of productivity and thermodynamic performance of metabolic pathways, Ind. Eng. Chem. Res. 47 (2008) 5669–5679.

[28] R. Rivero, M. Garfias, Standard chemical exergy of elements updated, Energy 31 (2006) 3310–3326.

[29] A. Ludovisi, Exergy vs. information in ecological successions: Interpreting community changes by a classical thermodynamic approach, Ecol. Model. 220 (2009) 1566–1577.

[30] J. Szargut, A. Valero, W. Stanek, A. Valero, Towards an international reference environment of chemical exergy. Available from: <http://www.exergoecology.com/papers/towards_int_re.pdf> (accessed on 23 December 2010).

[31] A. Martínez, J. Uche, Chemical exergy assessment of organic matter in a water flow, Energy 35 (2010) 77–84.

[32] AQSIQ (Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China), Technical Guides for Exergy Analysis (GB/T 14909-94), Standards Press of China, Beijing, 1994 (in Chinese).

[33] G. Bendoricchio, S.E. Jørgensen, Exergy as goal function of ecosystems dynamic, Ecol. Model. 102 (1997) 5–15.

[34] L. Luo, X.C. Wang, W.S. Guo, H.H. Ngo, Z. Chen, Impact assessment of excess discharges of organics and nutrients into aquatic systems by thermodynamic entropy calculation, J. Environ. Manage. 112 (2012) 45–52.

[35] A. Zaleta-Aguilar, L. Ranz, A. Valero, Towards a unified measure of renewable resources availability: The exergy method applied to the water of a river, Energy Convers. Manage. 39 (1998) 1911–1917.

[36] M.F. Dignac, P. Ginestet, D. Rybacki, A. Bruchet, V. Urbain, P. Scribe, Fate of wastewater organic pollution during activated sludge treatment: Nature of residual organic matter, Water Res. 34 (2000) 4185–4194.

[37] M.L. Quaranta, M.D. Mendes, A.A. MacKay, Similarities in effluent organic matter characteristics from Connecticut wastewater treatment plants, Water Res. 46 (2012) 284–294.

[38] MEPC (Ministry of Environmental Protection, PRC), Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB18918-2002), Standards Press of China, Beijing, 2002 (in Chinese).

[39] MEPC (Ministry of Environmental Protection, PRC), Environmental Quality Standards for Surface Water (GB3838-2002), Standards Press of China, Beijing, 2002 (in Chinese).