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Quantifying the electron-donating and -accepting capacities of wastewater for evaluating and optimizing biological wastewater treatment processes

*Xian-Bin Ying, Chen-Yi Tang, Wei Guo, Dong-Shen Sheng, Mei-Zhen Wang, Hua-Jun Feng**

Zhejiang Provincial Key Laboratory of Solid Waste Treatment and Recycling, School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China

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ABSTRACT

Biological processes have been widely used for the treatment of both domestic and industrial wastewaters. In such biological processes, pollutants are converted into pollution-free substances by microorganisms through oxidation-reduction reactions. Thus, how to quantify the internal oxidation-reduction properties wastewaters and seek out targeted countermeasures is essential to understand, operate, and optimize biological wastewater treatment systems. So far, no such approach is available yet. In this work, a novel concept of electron neutralization-based evaluation is proposed to describe the internal oxidation-reduction properties of wastewater. Pollutants in wastewater are defined as electron donor substances (EDSs) or electron acceptor substances (EASs), which could give or accept electrons, respectively. With such an electron neutralization concept, several parameters, i.e., electron residual concentration (R), economy-related index (E and E_r), and economical evaluation index (Y and Y_r), are defined. Then, these parameters are used to evaluate the performance and economic aspects of currently applied wastewater treatment processes and even optimize systems. Three case studies demonstrate that the proposed concept could be effectively used to reduce wastewater treatment costs, assess energy recovery, and evaluate process performance. Therefore, a new, simple, and reliable methodology is established to describe the oxidation-reduction properties of wastewater and assess the biological wastewater treatment processes.

Introduction

Biological wastewater treatment processes have been widely used for the treatment of both domestic and industrial wastewater. So far, a few issues, e.g., high energy investment and chemical requirement, remain with present researches and applications of biological processes, which are attributed to complex wastewater characteristics and inappropriate disposal methods. Hence, it is essential how to adequately understand wastewater characteristics and choose the appropriate wastewater treatment methods.

* Corresponding author.
E-mail: fenghuajun@mail.zjgsu.edu.cn (H.-J. Feng).

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In recent decades, an innovative and developing wastewater treatment becomes promising trends for cost reduction that uses one pollutant to eliminate another pollutant, such as anaerobic ammonia oxidation (Anammox) (Wang et al., 2019) and sulfate-reducing ammonia oxidation (SRAO) (Wang et al., 2017). Besides, recovering energy from wastewater is considered a promising way to replace traditional wastewater treatment processes to address their economic and environmental issues (Smith et al., 2014). However, there remains the issue that how to precisely estimate the energy recovery potential of the wastewater, optimize wastewater treatment strategies, and quantitatively describe that the newly developed process outshines the previous one. Since the determinations of the cost of treatment processes and the energy recovery capacity are usually time-consuming and laborious, the establishment of evaluation models is essential to process optimization and prediction of the new methods and processes.

Many researchers have attempted to develop models to describe the properties of wastewaters for assessment energy recovery potential and treatment costs, but no universal methodology has been provided. Shizas and Bagley (Shizas and Bagley, 2004) measured and calculated the energy content of wastewater by a bomb calorimetry method, leading to the connection between energy content and chemical oxygen demand (COD). However, Heidrich et al. (Heidrich et al., 2011) have claimed that no standard relationship to measured COD was observed in his study, but 13-14 kJ/g COD seemed to be the minimum energy content in the wastewater. Such a result was influenced by several factors. For example, some chemicals like urea did not reflect the real energy of wastewater, some substances could evaporate in the measurements, and other components like NO_3^- would consume the organic matter (OMs). Therefore, how to accurately evaluate the recoverable energy potential of wastewater needs to be reconsidered. Moreover, although various models for wastewater treatment processes have been established (Huang et al., 2013; Manoli and Samara, 2008), the models are usually aimed at one specific treatment process. A comparison of different processes is usually conducive to select the optimal processes, but no model has been established to compare the economic costs of different wastewater treatment processes yet.

The essence of most biological treatment is microorganisms or enzyme-mediated oxidation-reduction reactions, involving donating or accepting of electrons. Thus, we propose the hypothesis that wastewater actually could be vividly considered an electron warehouse for donating or accepting electrons. As most of the biological wastewater treatments and energy recovery methods are closely related to the electrons, it is theoretically feasible to develop electron-based models to evaluate the wastewater characteristics, treatment processes, and energy recovery. However, such a concept has not been proposed yet.

Therefore, a novel concept of electron-based evaluation is proposed in this study. First, contaminants in wastewater are uniformly re-defined as electron donor substances (EDSs) and electron acceptor substances (EASs), which are potential electron donors and electron acceptors respectively. With such a concept, several parameters i.e., electron residual concentration (R), economy-related index (E and E_r), and economical evaluation index (Y and Y_r), are defined. Then, these parameters are used to evaluate the wastewater characteristic, energy recovery, and processes optimization. Such an evaluation concept opens an avenue to generate novel and constructive ideas for reducing wastewater treatment costs.

1. Evaluation concept development

1.1. Proposal of the new concept

From the perspective of electron transfer, some chemicals such as sulfates, nitrates, and high valence metallic ions are the ultimate electron acceptors in biochemical processes (Li et al., 2019; Qian et al., 2017), whereas electron donors mainly consist of OMs, sulfides, low valence metals, and ammonia, etc. (Glodowska et al., 2020; Tian and Yu, 2020; Wei et al., 2017).

If we define the electron donor pollutants and electron acceptor pollutants in wastewater as EDSs and EASs, respectively, they are capable of neutralizing electrons based on thermodynamics (Kaganovich et al., 1992). We define this process as biological electron neutralization.

A series of common EDSs and EASs in wastewater are listed in Table 1. The electron equivalent of each substance is defined to quantitatively assess the electron-donating and -accepting capability of EDSs and EASs, respectively.

The number of EDSs (P, mol e^-/m^3) in wastewater that is used to neutralize EASs could be expressed below:

$$P = \sum_{1}^{i} e_i^+ p_i \quad (1)$$

where, e^+ i is the electron equivalent of EDS_i and p_i is the amount of EDS_i (g/m^3). The value of P represents the ability of all EDSs to deliver electrons to EASs. The types of EDSs, especially OMs, are complex in wastewater, but almost all EDSs (except NH_4^+-N, carbamide and, refractory OMs) in Table 1 can be oxidized by potassium dichromate (Cl^- needs to be masked). Hence, the content of EDSs is usually characterized by electron equivalent of the measured COD value (Cl^- needs to be masked). When there are substances such as ammonia or urea, their electron equivalents are also counted. Substances like F^- and Cl^- are generally not considered unless they participate in the electron neutralization.

Similarly, the amount of EASs (N, mol e^-/m^3) in wastewater can be expressed as follows:

$$N = \sum_{1}^{j} e_j^- n_j \quad (2)$$

where, e^- j is the electron equivalent of EAS_j and n_j is the amount of EAS_i (g/m^3). The value of N, represents the ability of all EASs to accept electrons. Although EASs such as PO_4^- can be reduced by biological processes (Crutchik et al., 2018; Figdore et al., 2018), physical or chemical methods are the most effective means to remove these pollutants. Therefore, these types of pollutants are also not considered in the model at the current stage, unless special functional microorganisms (e.g. phosphate-reducing bacteria (Dévai et al., 1988)) are utilized.

Table 1 – Common EDSs and EASs in wastewater.

	EDSs	electron equivalent (mol e^-/g)	EASs	electron equivalent (mol e^-/g)
VFAs	Acetic acid/CO_2	0.133	N_2O/N_2	-0.045
	Propionate acid/CO_2	0.15	O_2/H_2O	-0.0625
	Butyric acid/CO_2	0.167	NO_3^--N/N_2	-0.357
Sugars	Glucose/CO_2	0.133	NO_2^--N/N_2	-0.214
	Sucrose/CO_2	0.140	SO_4^{2-}/HS^-	-0.083
	Lactose/CO_2	0.140	Fe^{3+}/Fe^{2+}	-0.018
	Xylose/CO_2	0.133	H^+/H_2	-1.000
	Galactose/CO_2	0.133	HCO_3^-/ Acetic acid	-0.066
	Fructose/CO_2	0.133	$S_2O_3^{2-}/HS^-$	-0.071
	Soluble starch/CO_2	0.133n	Cr^{6+}/Cr^{3+}	-0.0577
Others organic	Fibers/CO_2	0.133n	PO_4^-/H_3P*	
	Amino acids/CO_2	0.22-0.35		
	Carbamide/CO_2, NH_3	0		
	Carbamide/CO_2, N_2	0.099		
Inorganic	HS^-/SO_4^{2-}	0.242		
	NH_4^+-N/ N_2	0.214		
	NH_4^+-N/ NO_2^--N	0.428		
	H_2/H_2O	1.000		
	NO_2^--N/ NO_3^--N	0.143		
	Fe^{2+}/Fe^{3+}	0.018		
	S /SO_4^{2-}	0.1875		
	$S_2O_3^{2-}/SO_4^{2-}$	0.036		
	COD/CO_2†	0.125		

* Can be used as EASs when special microbes are applied;
† In this paper, COD refers to COD_{Cr}, and in most cases, they are OMs or represent inorganic reducing substances that can be oxidized by potassium dichromate.

In addition, according to thermodynamics, electrons could only spontaneously flow from low potential to high potential. There, the electron neutralization of wastewater involved in this study could only happen based on the thermodynamic principles and with microorganisms as catalysts. Biological processes that require additional energy (except for aeration for oxygen supply) are not considered here.

1.2. *Definition of electronic residual concentration (R)*

After the neutralization of EDSs and EASs, there are generally EDSs or EASs remaining in the wastewater. Since the wastewater is still able to donate or accept electrons after electron neutralization, the electron residual concentration (R, mol/m^3) is defined to evaluate the characteristic of wastewater as follows:

$$R = \frac{1}{(\sum_1^n V_n)}\left(\begin{bmatrix} e_1^+ p_1 \\ e_2^+ p_2 \\ \vdots \\ e_i^+ p_i \end{bmatrix} \times \begin{bmatrix} V_1 \\ V_2 \\ \vdots \\ V_n \end{bmatrix} + \begin{bmatrix} e_1^- n_1 \\ e_2^- n_2 \\ \vdots \\ e_j^- n_j \end{bmatrix} \times \begin{bmatrix} V_1 \\ V_2 \\ \vdots \\ V_n \end{bmatrix}\right) \quad (3)$$

where, V_n (m^3) represents the volume of wastewater n. e^+ iis the electron equivalent of EDS_i and p_i is the amount of EDS_i (g/m^3). e^- j is the electron equivalent of EAS_j and n_j is the amount of EAS_i (g/m^3).

If the R-value is equal to zero, there are no additional chemicals required for the complete treatment of the wastewater. Therefore, for these wastewaters, the treatment processes without extra chemicals or energy could be theoretically achieved (Yan et al., 2017). A positive R-value indicates that the EDS pollutants in the wastewater require further treatment or could be used for bioenergy recovery (e.g. CH_4 and electricity) when the EDSs are biodegradable OMs. A negative R-value indicates additional electron donors (e.g. sulfur and methanol) need to be added for removing the rest EASs. Therefore, the R-value could simply and quantitatively indicate a characteristic of the wastewater, i.e., whether it needs extra electron acceptor or electron donor chemicals and how many chemicals it requires for its complete treatment. Moreover, the R-value could quantitatively indicate the bioenergy recovery potential when the main EDSs are biodegradable OMs.

1.3. *Definition of economy-related index (E and E_r)*

As the R-value quantitatively indicate the amount of the remaining EDSs and/or EASs, the amount of required electron donors and acceptors could be determined for complete removal of those remaining pollutants. The concentration of additional electron donors and acceptors in the treatment process are defined as R_P and R_N, respectively, and the economic value of per mole of R_P and R_N are defined as α and β, respectively. Then, the total costs of different wastewater treatments

could be expressed as:

$$E = \sum_{1}^{n} |\alpha_n R_{P_n}| + \sum_{1}^{m} |\beta_m R_{N_m}| \quad (4)$$

where, E (mol e^-/m^3) represents the sum of processing costs of per cubic of the wastewater; R_{Pn} (mol/m^3) is the final concentration of additional electron donors n, such as the organic carbon source; and R_{Nm} (mol/m^3) is the final concentration of additional electron acceptors m, such as oxygen. α_n (dimensionless) is the economic coefficient of added electrons donor n, which is the cost ratio of an additional electron donor (α_{sn}) and methanol ($\alpha_{methanol}$) that provide the same concentration of electrons, i.e., $\alpha_{sn}/\alpha_{methanol}$; while β_m (dimensionless) is the economic coefficient of added electron acceptor n, which is the cost ratio of an additional electron acceptor (β_{sm}) and oxygen (β_{oxygen}) that accept the equal amount of electrons, i.e., $\beta_{sm}/\beta_{oxygen}$. In this paper, we define both the economic coefficient of methanol and the economic coefficient of oxygen (energy for aeration) as 1. For example, suppose that the price of acetate that donates the same number of electrons is 1.3 times than that of methanol, then the α is taken as 1.3 when using acetate as an additional electron donor.

Similarly, for the energy recovery of organic wastewater, the maximum potential for energy recovery is theoretically equal to R when it is a very positive value. After recovery the energy, organic wastewater always needs to be further processed for excess EDSs removal. Hence, the sum of the energy recovery potential (E_r) of the wastewater could be expressed as Eq. (5).

$$E_r = \sum_{1}^{a} |\lambda_a \gamma_a R_a| - \sum_{1}^{a} \left| \sum_{1}^{m} \beta_m (1-\lambda_a) R_a \right| \quad (5)$$

here, R_a represents the concentration of recovered electrons in the form of matter or energy a. λ_a represents the recovery efficiency of electrons (range 0–1). γ_a represents the energy coefficient of the recovered electrons. Here γ_a of methanol is defined as 1, then γ_a of other substitutes are the ratios of their energy densities (γ_{sa}) to methanol ($\gamma_{methanol}$), i.e., $\gamma_{sa}/\gamma_{methanol}$. Ideally, λ_a could be 1 when all electrons are recovered. As the R_a could not be completely recovered, the rest R_a requiring treatment could be presented as $\sum_{1}^{a} |\sum_{1}^{m} \beta_m (1-\lambda_a) R_a|$. Therefore, a higher E_r-value is associated with a better energy recovery potential.

The model of E_r is suitable for organic wastewater. For inorganic EDSs (e.g. S^{2-}, NH_4^+-N), energy recovery is possible but difficult at this stage. Resource recovery is a strategy for these EDSs and would be considered in the future model optimization.

1.4. *Definition of evaluation index (Y and Y_r)*

As R-value indicates the remaining electrons that require treatment after electron neutralization in the wastewater, $\alpha|R|$ (for the remaining EDSs) or $\beta|R|$ (for the remaining EASs) could simply represent the minimum cost of the wastewater treatment. If we define the $\alpha|R|$ or $\beta|R|$ as the quantification benchmark, then the merits or demerits of an existing treatment process can be quantitatively judged using the ratio of the $\alpha|R|$ or $\beta|R|$ to the E, which can be defined as the economical evaluation index, Y:

$$Y = \frac{\alpha|R|}{\sum_{1}^{n} |\alpha_n R_{P_n}| + \sum_{1}^{m} |\beta_m R_{N_m}|} \text{ or } Y = \frac{\beta|R|}{\sum_{1}^{n} |\alpha_n R_{P_n}| + \sum_{1}^{m} |\beta_m R_{N_m}|} \quad (6)$$

When EASs and EDSs contaminants are present in wastewater simultaneously, the process is considered to be more efficient if the Y-value of the process for treating wastewater is closer to a constant $\alpha/\sum_{1}^{n}\alpha_n$ or $\beta/\sum_{1}^{m}\beta_m$. Conversely, the more the Y-value close to 0, the higher the costs of the processes.

Similarly, the maximum potential for energy recovery is theoretically equal to $\gamma|R|$ when R is positive in organic wastewater. If we define the maximum potential as the quantification benchmark, then the energy recovery potential of organic wastewater could be expressed as Y_r:

$$Y_r = \frac{\sum_{1}^{a} |\lambda_a \gamma_a R_a| - \sum_{1}^{a} \left| \sum_{1}^{m} \beta_m (1-\lambda_a) R_a \right|}{\gamma|R|} \quad (7)$$

Here, if the Y_r of organic wastewate$_r$ is closer to $\sum_{1}^{a} |\gamma_a R_a|/\gamma|R|$, it is considered to be more beneficial for energy recovery. Conversely, when the Y_r-value is close to or even below 0, the wastewater is considered to have little energy recovery potential.

2. Results and discussion

To verify the simplicity and practicality of this evaluation method, three cases on terms of treatment strategies, energy recovery assessments, and process evaluations were analyzed via the proposed parameters. The parameter validations demonstrated the important role of the electron neutralization concept in wastewater treatment processes.

2.1. *Electron neutralization between wastewaters*

At this stage, most pollutants in wastewater are treated separately, which generally results in high-cost and inefficient wastewater treatments. Therefore, synergistic removal of pollutants is probably a promising method whether it is in current stage or in the future. Here, electron neutralization between wastewaters was proposed for cost reduction of wastewater treatments.

Here, we selected two typical wastewaters for model analysis. One is slaughterhouse wastewater with a COD of 1820 g/m^3 reported by Pozo et al. (Del Pozo and Diez, 2005), and 96% of COD was removed through the aerobic process. The essence of aerobic treatment is that microorganisms transfer electrons from OMs to oxygen, which causes energy consumption issues. However, if the electrons were transferred to the EASs required to be treated, such as NO_3^- or NO_2^-, it would be possible to reduce the costs of pollutant removal of both EDSs and EASs at the same time. Hence, a stainless steel wastewater mainly containing EASs, was chosen from Appendix A **Table S1** for electron neutralization with the slaughterhouse wastewater. Detailed wastewater characteristics and some assumptions for this base-case were listed in Table 2. As the concentration of sulfate was not provided in Pozo's study, sulfate

Table 2 – Wastewater characteristics and assumptions for an electron neutralization.

Wastewater Characteristics		
Characteristics	Slaughterhouse wastewater	Stainless steel wastewater
COD	1820 g/m^3	65.1 g/m^3
NO_3^--N	-	455.5 g/m^3
NO_2^--N	-	69.0 g/m^3
SO_4^-	-	155.4 g/m^3
Other Assumptions		
A. The electron footprint in microbial metabolism is not considered in this case; B. Both α and β are 1; C. Electron neutralization process is complete; D. The volumes of the wastewaters are both 100 m^3; E. The removal process for each contaminant is considered independent.		

Table 3 – R and E_r of wastewater before and after electron neutralization.

Parameters	Slaughterhouse	Stainless steel	Mixed*
R (mol/m^3)	227.50	-182.14	45.36
αR_p (mol/m^3)	0	182.14	0
βR_n (mol/m^3)	-227.50	0	-45.36
E (mol/m^3)	227.50	182.14	45.36
Total treated electrons (mol)	40964#		9072

* A mixed wastewater from the slaughterhouse and the stainless steel plant;
\# The value of total treated electrons is linear with total processing costs.

of the slaughterhouse wastewater was not considered in this case.

As shown in Table 3, the R of EDSs in slaughterhouse wastewater was 227.50 mol/m^3, whereas the R of EASs in the stainless steel wastewater was calculated to be -182.14 mol/m^3. However, the R of mixed wastewater obviously decreased to 45.36 mol/m^3 after electron neutralization. When considering the amount of wastewater, electrons to be treated in the mixed wastewater are 9072 mol based on a total volume of 200 m^3 of the mixed wastewater, which was only 22% of that the sum of the separate treatments. The detailed calculation process refers to **Supplementary materials**.

Obviously, separate treatment of these wastewaters would increase the costs of the whole preprocess under such a specific condition. Although the simulation results were calculated under the assumptions, EDSs and EASs can be collaboratively removed under the action of functional microorganisms. These results indicated that the neutralization of EDSs and EASs greatly reduced the total cost.

As shown in Appendix A **Table S1**, industrial wastewater frequently contains high levels of contaminants with a simple chemical composition. Unreasonable treatment strategies of these wastewaters greatly increase the treatment costs. Therefore, the introduction of the electron neutralization concept that aims to co-process EDSs and EASs pollutants between wastewaters of different characters will be indispensable for efficient and economical wastewater treatment in the future.

2.2. *Energy recovery evaluation*

Wastewater, especially organic wastewater contains an enormous amount of potential energy (Lee et al., 2013). COD was frequently considered the best parameter to represent the potential energy content of organic wastewater (Heidrich et al., 2011). However, EASs-like containments in organic wastewater also have the potential to compete for electrons and reduce the maximum recovery potential, but it was usually neglected. This issue probably leads to inaccurate energy assessment of some organic wastewater, resulting in treating wastewater in an improper and high-cost way.

Hence, energy recovery potential evaluation based on electron neutralization between EDSs and EASs was proposed in this section. A base-case of hydrogen and methane production in a typical two-phase reactor based on electron neutralization is provided. In the instance calculation, sugar wastewater, containing different concentrations of SO_4^{2-}, process parameters, and some ideal assumptions was provided in Table 4, to more accurately assess the energy recovery potential of organic wastewater in the presence of EASs.

When only the COD value was used to assess the energy recovery potential of the wastewater, the E_r was 402.78 mol/m^3, while the Y_r was 0.64 (Table 5). With the increase of SO_4^{2-} concentration, R of the organic wastewater gradually decreased, indicating that the maximum potential value of energy recovery also decreased. Since the same final effluent COD concentration was set, the potential methane recovery content reduced as the influent COD concentration of Phase 2 decreased. Therefore, Y_r kept a downward tendency from 0.64 to 0.56 with the increase of SO_4^2 content, demonstrating a negative drop in energy recovery potential.

Essentially, the recovery of energy from wastewater is the recovery of electrons in OMs. As the above results show, energy recovery potential based on electron neutralization from organic wastewater will always be lower than that based only on the COD content in wastewater when there is a great deal of EASs.

The model and Case 2 indicate that although some of the organic wastewaters are provided with high COD concentration, they are still not a priority for energy recovery. Because in the actual production process, energy recovery from organic wastewater still puts the COD value first, resulting in increased costs of subsequent treatment of remaining EDSs or EASs. However, when the inhibitory effect of a large number of EASs and costs of subsequent wastewater treatment are considered, the costs of EASs after electron neutralization or remaining EDSs to be further treated can be circumvented. Therefore, calculating the concentration of residual electrons in organic wastewater enables a more accurate assessment of the energy recovery potential of high-strength organic wastewater.

Table 4 – Base-case assumptions of energy evolution using typical two phase.

Sugar wastewater Characteristics						
	Characteristic			Concentration		
	COD			6000 g/m^3		
	SO_4^{2-}			300, 600, 900, 1200, 1500 g/m^3		
	A Two-phase Process parameters					
	Phase 1			Phase 2		
SO_4^{2-} g/m^3	Influent COD g/m^3	COD Rem.% (H_2+SO_4^{2-})[#]	SO_4^{2-} Rem.%	Influent COD g/m^3	COD Rem.%	Effluent COD g/m^3
-	5000	7.70	-	4615.0	84.71	705.6
300	5000	7.70+3.98	100%	4416.0	84.02	705.6
600	5000	7.70+7.97	100%	4216.5	83.27	705.6
900	5000	7.70+12.00	100%	4015.0	82.43	705.6
1200	5000	7.70+15.94	100%	3818.0	81.52	705.6
1500	5000	7.70+19.91	100%	3619.5	80.51	705.6
Other assumptions						
A. The electron footprint in microbial metabolism is not considered in this case; B. Both α and β are 1, and $\gamma(CH_4)$ and $\gamma(H_2)$ is 0.3[*]; C. A substrate conversion rate of 7.70% for hydrogen and 84.71% for methane are chosen according to the previous literature (Bing et al., 2013); D. A maximum theory yield of 0.016 mol CH_4/g COD and 0.020 mol H_2/g COD. E. Sulfate reduction and hydrogen production processes are considered independent and do not affect each other. F. Any pump energy, alkalinity supplement, and temperature maintenance are not considered.						
[#] COD removal rate for hydrogen production and sulfate reduction, respectively; [*] The value of $\alpha(H_2)$ is calculated based on energy density. Energy density: 242 kJ/mol of hydrogen, 801 kJ/mol of methane.						

Table 5 – Energy recovery evolution on organic wastewater with various SO_4^{2-} content.

SO_4^{2-} (g/m^3)	R (mol/m^3)	$\Sigma\lvert\lambda_n\gamma_n R_n\rvert$(mol/m^3)	$\sum \lVert\alpha_n R_{P_n}\rvert + \lvert\beta_n R_{N_n}\rVert$ (mol/m^3)	E_r (mol/m^3)	Y_r (mol/m^3)
-	625	490.98	88.2	402.78	0.64
300	600.1	466.10	88.2	377.90	0.63
600	575.2	441.19	88.2	352.99	0.61
900	550.3	416.01	88.2	327.81	0.60
1200	525.4	391.36	88.2	303.16	0.58
1500	500.5	366.57	88.2	278.37	0.56

2.3. *Processes evaluation*

The anaerobic ammonium oxidation was sought after by both researchers and engineers in the wastewater treatment field (Ding et al., 2018), but its superiority has always been a qualitative comparison. Therefore, quantitatively describing the differences between a new process and an old one allows the selector to intuitively know which process is more suitable. Hence, electron-based evaluations between different processes were proposed in this section.

Here, three typical biological nitrogen removal process processes were chosen for comparison based on an electron neutralization-based evaluation system. The base-case assumptions of wastewater characteristics processes parameters and other key preconditions were listed in Table 6.

As shown in Table 7, the R of the wastewater was 65.67 mol/m^3 when a removal rate of 95% for COD and 98% for NH_4^+-N. When traditional aerobic OMs oxidation + Nitrification/Denitrification process was used, the E- and Y-values of the wastewater according to Eqs. (4) and (6) were 85.61 and 0.77 mol/m^3, respectively. However, the E of wastewater treated by the aerobic OMs oxidation + Single reactor high activity ammonium removal over nitrite-anaerobic ammonia oxidation (SNAAO) process went down to 65.80 mol/m^3, while the Y-value was extremely close to $\beta/\sum_1^m \beta_m = 1$, which is the theoretical maximum Y-value. The results of the verification of the parameters prove that the aerobic OMs oxidation + SNAAO process is an ideal process for treating the wastewater theoretically. However, as a commonly used process in WWTPs, Y of wastewater treated by Anoxic/Oxic (A/O) was up to 0.98 in this case, illustrating that the aerobic OMs oxidation + SNAAO process did not significantly outshine the mostly used A/O process. Such a result was ascribed to the high C/N in the assumed wastewater. However, for the low C/N wastewater, the aerobic OMs oxidation + SNAAO process

Table 6 – Base-case assumptions of process comparison.

Wastewater Characteristics					
Characteristic		Concentration			
COD		500 g/m^3			
NH_4^+-N		30 g/m^3			
Process parameters					
①	Aerobic OMs oxidation + Nitrification/Denitrification	COD Rem.% 95	Nitratification N Rem.% 98	Denitrification N Rem.% 90	Reflux ratio% /
②	Aerobic OMs oxidation + SNAAO*	COD Rem.% 95	Nitritification N Cov.% 50	Anammox N Rem.% 90	Reflux ratio% /
③	Anoxic/Oxic	COD Rem.% 95	Nitratification N Rem.% 98	Denitrification N Rem.% 90	Reflux ratio% 100%
Other assumptions					
A. The electron footprint in microbial metabolism is not considered in this case; B. Both α and β are 1; C. Any pump energy, alkalinity supplement, and temperature maintenance are not considered.					
* The SHARON-ANAMMOX (SNAAO) process					

Table 7 – Comparison of three processes.

Parameters	①	②	③
R (mol/m^3)	65.67*	65.67*	65.67*
αR_p (mol/m^3)	76.16	65.80	66.71
βR_n (mol/m^3)	-9.45	0	0
E (mol/m^3)	85.61	65.80	66.71
Y	0.77	0.998	0.98

* The actual minimum cost under condition of COD Rem.=95% and Nitratification N Rem.=98%.

manifests a huge advantage when additional carbon sources are necessary (Case S1 in Appendix A). A similar conclusion was previously drawn by McCarty (2018), verifying the validity of the electron neutralization-based evaluation methodology. The detailed calculation process is described in Appendix A.

Since the traditional wastewater treatment process evaluation is often comparing the operation costs of the already established WWTPs or devices, there remains the issue that evaluation procedure is considerably time-consuming and laborious. Although various models for wastewater treatment processes like energy consumption and pollutant degradation have been established, the model is frequently aimed at one specific treatment process and is very complicated. Hence, such a Y-based evaluation for wastewater process evaluation was proposed and established for simple and fast comparison processed based on the concept of electron neutralization.

2.4. *Further discussions for pros and cons*

According to the above cases, a wastewater treatment strategy based on electron neutralization was proposed. To optimize wastewater treatment, the EDSs and EASs pollutants inside the wastewater are assumed to achieve electron neutralization as completely as possible, while for wastewater containing only EDSs and EASs pollutants, electron neutralization between these wastewaters is primarily considered. If the R of the organic wastewaters is still over 0 after electron neutralization, then energy recovery from the wastewaters was considered before they are treated to meet the emission standards. If the R-value is below 0, further advanced treatment is considered when the EASs pollutants do not meet the emission standards.

In summary, there are three practical functions based on the electron neutralization evaluation system. First, it can be applied to the optimization of the wastewater treatment scheme. Calculation results of the electron neutralization between wastewaters showed that electron neutralization-based schemes adhering to the principle of synergistic removal of electron-donating and -accepting pollutants, which is more cost-effective than conventional processes. Second, assessing the energy recovery potential of organic wastewater using electron neutralization is more accurate than direct assessment using COD as a standard. Finally, it can be used for the evaluation of processes. For the three typical denitrification processes, the processes based on the electron neutralization principle are more economical and produce less secondary pollution. The introduction of such a new concept has extraordinary significance in the wastewater treatment systems, ranging from the design and selection of optimal processes to the reduction of global wastewater treatment costs. In general, such an electron neutralization concept opens an avenue to generate benefits to the environment, energy, and economy.

Nevertheless, there are still several drawbacks that need to be improved before the electron neutralization evaluation system is implemented. First, the electron neutralization of EDSs and EASs in wastewater and between multiple wastewaters are proposed based only on microbial redox in this paper, which is limited for the current wastewater treatment field. Hence, this evaluation system needs to be brought to completion with pure chemical redox (e.g., advanced oxidation),

physical treatments and even thermodynamically unfavorable electron neutralization by inputting energy (e.g., electrolysis). Second, the *E*-values of different processes is mainly related to the content of EDSs and EASs in the treated wastewater, which ignores the different energy consumption of pumps of different processes. Although the total power consumption of the pumps can handle about 1%–5% of the total cost of domestic wastewater or industrial wastewater, it is still considerable when combination processes are used. Therefore, the establishment of a relationship between the pumping energy and *E* will be considered in subsequent studies to improve the evaluation system. Thirdly, in many cases, H_2O (or H^+, OH^-) takes part in oxidation and reduction reaction. For example, algae could use H_2O as an electron donor for organic matter synthesis and nutrients recycling (Ji et al., 2020). Microbes in the microbial electrosynthesis system could use electrodes as electrode donors, and the initial and electron donor is also H_2O (Bian et al., 2020), or any substances that provide electrons at the anode. For chemical treatments, using H_2O as an electron donor or electron acceptor is more common, such as photocatalysis (Rueda-Marquez et al., 2020) and electrocatalysis (Zhou et al., 2020). Biological or chemical processes involved H_2O as the electron donor or acceptor need to be emphasized. Finally, small portion pollutants that are difficult to remove by the oxidation-reduction reactions based on microbial metabolisms, such as phosphorus, are not considered in the evaluation system and may be added to the evolution system by equivalent conversion coefficients in the future.

3. Conclusions and outlooks

This paper presents the concept of electron neutralization of wastewater for the first time, with new concepts such as EDSs, EASs, electron residual concentration (*R*), economy-related index (*E* and E_r), and economical evaluation index (*Y* and Y_r). Based on cheap and effective microbial methods, the realization of electron neutralization has certain feasibility, whether at current status or in the future time. Theoretical calculations indicate that the electron neutralization occurs between different wastewaters with the opposite nature saves considerable energy and chemicals. Also, electron neutralization-based energy recovery evolution reconsiders if organic wastewater is worth recovering biogas.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.09.026.

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