Making Waves

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Making Waves: A sea change in treating wastewater – Why thermodynamics supports resource recovery and recycling

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ABSTRACT

Entropy is a concept defined by the second law of thermodynamics. Applying this concept to the world we live in, entropy production must be minimized and negentropy (negative entropy production) should be accelerated, in order to produce a healthy and stable ecological system. The present wastewater treatment, however, contributes to entropy production. This means that conventional wastewater treatment, without recovery of resource and energy, will gradually but inevitably contribute to a deteriorating ecological balance. When the self-cleaning ability of the natural ecological system is limited, the need to develop sustainable wastewater treatment in order to delay entropy production and accelerate negentropy becomes urgent. Resource and energy recovery from wastewater should be the first priority, as they can contribute significantly towards minimizing entropy production and accelerating negentropy. Sustainable wastewater treatment must focus on recovering recyclable high value-added organic chemicals from wastewater and/or excess sludge to minimize entropy production caused by methane (CH_4, once combusted, is converted into CO_2 - an even higher substance in entropy) via anaerobic digestion. Instead of CH_4, thermal energy present in the effluent can be utilized for heating/cooling buildings and also for drying excess sludge towards incineration to recover more energy. Overall, this can lead to a carbon-neutral operation and even creating a "carbon sink" could be possible for wastewater treatment.

1. Introduction

Entropy, a concept derived from the study of thermodynamics, describes the tendency of any closed system to increasingly descend into disorder or chaos, leading to the collapse of the system (Marchettini et al., 2008). But thanks for the solar energy, there is also a reverse process known as negative entropy, or negentropy in the earth ecosystem. This can occur in various forms of material regeneration such as photosynthesis, mineral enrichment, sedimentation and mineralization, etc. (Schrödinger, 1944). Clearly, a stable ecological system requires the recycling or neutrality of entropy production, and the promotion of negentropy, as shown in Fig. 1a (the green cycle). In recent years, the concept of entropy has been applied to environmental quality assessment (Diaz-Mendez et al., 2013; Luo et al., 2017), microbiology (Nijman, 2020; Todhunter et al., 2018), novel materials (Albedwawi et al., 2021; Biswas et al., 2020), machine design (Yu et al., 2021; Ziya Sogut, 2021), and a range of other areas. In the environment-related fields, negentropy is applied as an indicator of sustainability (Artuzo et al., 2021; Pelorosso et al., 2017; Saraswat and Digalwar, 2021)

While civilization has developed to a degree that brings comfortable and elevated lifestyles to many, it has also brought abnormal dissipation of resource and energy; and this, in turn, has resulted in accelerated entropy production which, inevitably, leads to the destruction of the ecological balance. As a pollutant discharged by human beings, wastewater inevitably leads to entropy production. Wastewater and its treatment, therefore, can and should be analyzed from the perspective of entropy, to search for more sustainable approaches.

Wastewater treatment is a form of biomimicry, including both anaerobic and aerobic processes, which enhances the self-cleaning capacity of a river in an engineered system by increase in aeration, mixing and biomass. This leads to extra entropy production due to consumption of energy and chemicals, which often leads to the phenomena of "destroying energy with energy" and "pollution transfer". Conventional wastewater treatment (CWWT), for example, focuses on removing organic carbon, nitrogen and phosphorus. As a result, potential organic energy and nutrients are often destroyed or wasted, which accelerates

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entropy production and leads to unsustainable use of resources and energy (Artuzo et al., 2021). Thus, CWWT is actually a process that both accelerates entropy production of natural substances (material/element decay) and delays negentropy (material/element regeneration), as shown in Fig. 1a (the red cycle). This increase in entropy inevitably results in both environmental degradation and resource depletion (Marchettini et al., 2008).

To lower the risk of entropy production in managing wastewater, sustainable wastewater treatment (SWWT) will need to be developed. How can this be achieved? Perhaps through the study of entropy itself.

2. Wastewater treatment and entropy

As mentioned above, wastewater treatment is a process of entropy production, mainly reflected in the material/energy conversion during treatment, which can be summarized as follows:

(i) at the material level, most organic substances (low-entropy substances such as carbohydrates, proteins, fats, etc.) in the influent are gradually decompose into a large number of small, disorganized inorganic, often gaseous substances (including high-entropy substances such as CO_2 and H_2O) by microbial metabolisms (Rapf and Kranert, 2021).

(ii) at the energy level, the high-grade energy in the organic substances is converted into the low-grade energy by microorganisms, which greatly reduces material availability (Rapf and Kranert, 2021). Macroscopically, this is a metabolic process in which microorganisms continuously dissipate energy in order to form new biomass and to maintain the complex cell system.

Enhanced microbial activities transform many of low-entropy pollutants that are discharged with wastewater into relatively stable high-entropy substances. The result of this process is accelerated entropy production and retarding negentropy, due to the fact that resource and energy recovery are not involved. Both of them result in the system gradually deviating from the natural entropy cycle (the red cycle illustrated in Fig. 1a). If additional materials and/or energy are used to achieve pollutant degradation, entropy production would be accelerated further, which can cause a much wider range of material and energy imbalances. This would deepen the deviation of the natural entropy cycle, until the natural ecological system begins to collapse eventually.

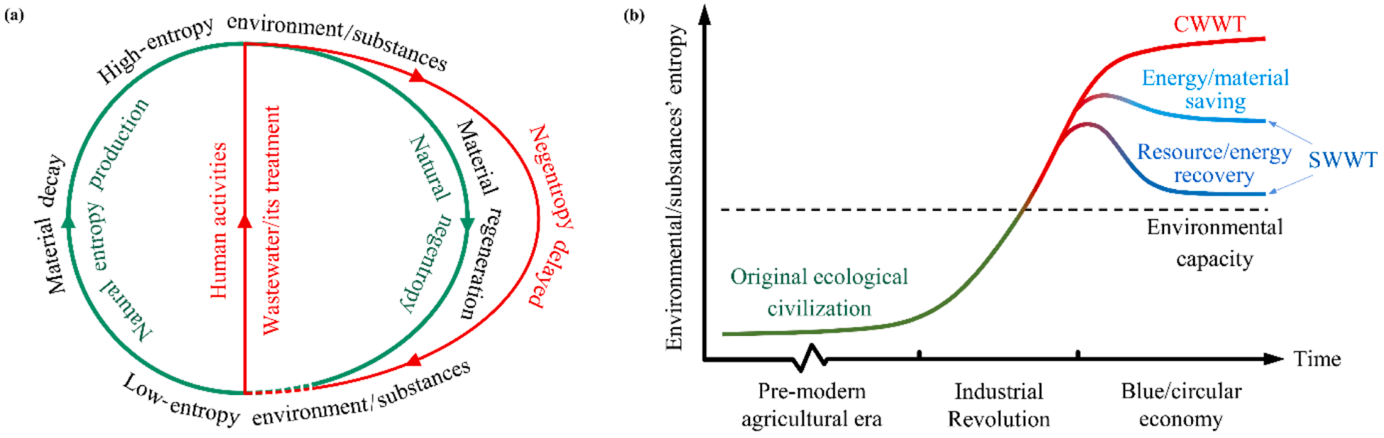
For this reason, wastewater treatment should aim to follow the natural entropy cycle, avoiding entropy production as much as possible and creating opportunities for negentropy to occur. In order to achieve this, approaches to developing synthetic and nondegradable materials for removing pollutants should be abandoned, as such materials tend to produce entropy in significant quantities and it is difficult to recycle them. Clearly, recyclable materials should be developed and applied to achieve negentropy.

3. Resource/energy recovery and negentropy

In the pre-modern agricultural era, human beings grew and fertilized crops with their own excreta, and waste/wastewater was purified by natural processes. During these processes, which invisibly conformed to the natural cycle of entropy, nutrients (C, N, P, K, etc.) and energy were recycled in exchanges between people and farmlands; thus, an ecological balance was maintained, not unlike the balance of the naturally occurring system. This state produced a harmonious coexistence between people and nature, which is now referred to as the “original ecological civilization”, and is illustrated Fig. 1b (the green curve). Regrettably, since the beginnings of the Industrial Revolution in Europe, humans have deviated more and more from this course, gradually replacing it with a more modern lifestyle, to the detriment of the environment.

The urbanization that accompanied the Industrial Revolution produced a mass system of modern toilet and sewer systems in modern cities, which resulted in the original ecological system being almost completely demolished. As a result, the nature-based habit of “excreta returning to farmlands” came to an abrupt halt, especially after the introduction of the Haber-Bosch process. Under the new systems, both domestic and industrial wastewater began to flow into rivers, lakes and oceans, accelerating entropy production, with the flushed-away nutrients and energy delaying the process of negentropy. Modern wastewater treatments have been able to improve both the hygiene and environmental health of cities, but they have also had the effect of intensifying entropy production.

Clearly, both accelerated entropy production and delayed negentropy, caused by the treatment of wastewater as well as wastewater itself, endanger the balance of the ecological system. It is therefore necessary for CWWT to be converted into SWWT in order to facilitate the effects of negentropy. Resource and energy recovery from wastewater treatment will contribute effectively to this process.



Entropy— material decay, describing the degree of unsustainability for a system;
Negentropy— material regeneration, indicating the degree of sustainability for a system.
CWWT— conventional wastewater treatment;
SWWT— sustainable wastewater treatment.

Fig. 1. Entropy cycle and ecological balance: a. natural entropy cycle (the green circle) & accelerated entropy production and delayed negentropy by wastewater and its treatment (the red half oval); b. entropy change tendency in different developed phases of human beings.

4. Sustainable wastewater treatment (SWWT) in context

In order to achieve SWWT, enhancing the input-output ratio of wastewater treatment would be the crux of wastewater treatment. In this way, delaying entropy production and accelerating negentropy could be associated with saving carbon and energy and recovering resource and energy from wastewater treatment, respectively. It is worth noting that the latter must be a priority in developing sustainable wastewater treatment (SWWT). Progress in this regard has already begun, and some global activities like phosphate/organic recovery, net zero carbon operation (carbon neutrality), etc. are already being implemented.

4.1. Approach to delaying entropy production

Due to the growth of human population, self-cleaning bodies of water are becoming less and less available near city's areas. Thus, both carbon and energy saving have become a major driving factor in developing sustainable wastewater treatment (SWWT). For this reason, anaerobic ammonia oxidation (ANAMMOX) and aerobic granular sludge (AGS) have been defined as the main technologies of wastewater treatment for the next generation (van Loosdrecht and Brdjanovic, 2014). However, both ANAMMOX and AGS are limited in their ability to alleviate entropy production. Because of this, accelerating negentropy is of the utmost importance in SWWT, with resource and energy recovery playing a key role.

4.2. Accelerating negentropy by resource and energy recovery

Both resource recovery and energy capture from wastewater treatment can contribute significantly to negentropy. The former can directly improve the sustainability of substances and reduce waste contaminating the natural environment, and the latter can make use of the potential energy present in wastewater. Phosphate recovery, for example, is of considerable importance in creating negentropy, as phosphate is an essential compound for P-fertilizer production (Chrispim et al., 2019).

The recovery and reuse of organic compounds can strongly contribute to decreases in entropy production (except for the anaerobic digestion of excess sludge, which will be discussed below). For this reason, recovery should be oriented to explore the recycling of high value-added chemicals like PHA, EPS/alginate, etc., which would create a sustainable approach and also aid in developing a blue/circular economy (van Loosdrecht and Brdjanovic, 2014).

Indeed, environmental sustainability can be strengthened by the continuous recycling and reuse of recovered resources and energy (Ghisellini et al., 2016). However, there is one important issue here that needs to be addressed: the prioritizing of resource and energy recovery. Regarding energy recovery, the conversion of chemical energy from excess sludge via anaerobic digestion (AD) is the most commonly used technology. However, this process results in high entropy production, as organic substances are converted into CH_4 and then, once combusted, into CO_2 - an even higher substance in entropy. Moreover, CH_4 leakages also increase the greenhouse gas (GHG) effect, as CH_4 is 28 times more potent than CO_2 (Chen et al., 2021). Clearly, the conversion of organics into CH_4 via AD is not a sustainable approach to SWWT, from the viewpoint of negentropy.

Theoretically, there is 9–10 higher chemical energy in wastewater than electricity demand for aerobic treatment (Shizas et al., 2004). In practice, however, only about 13% of the theoretical chemical energy could be converted to electricity and heat by AD with combined heat and power (Hao et al., 2019a). On the other hand, there is a large amount of residual thermal energy in the effluent of wastewater treatment plants (WWTPs), about 9 times higher in practice than converted chemical energy (Hao et al., 2019a), which can be used as an effective way to delay entropy production. Due to the high coefficient of performance (COP=3–5) for water source heat pump (WSHP), more thermal energy can be obtained than input electricity demand, which has been extensively applied for heating/cooling buildings in Europe and also defined as a main approach to carbon neutral operation of WWTPs (Pokhrel et al., 2022; Spriet et al., 2020). It is worth noting that thermal energy might be the most effective substitute for a low-temperature drying process of excess sludge prior to incineration (Hao et al., 2020). In most cases, thermal energy is able to meet the needs of carbon-neutral (or net zero carbon) operation of WWTPs in full, and can also form a significant "carbon sink" for carbon emissions trading (Hao et al., 2019b). Also, the effluent that remains after thermal energy has been extracted can reduce ecological risks when discharged into receiving waters during the winter season.

Although other thermochemical processes, like gasification, pyrolysis and even carbonization, have also been studied and evaluated as potential approaches to handling excess sludge (Syed-Hassan et al., 2017), incineration is relatively mature and has been practiced for decades in Europe and is also being applied in China. When gasification, pyrolysis and carbonization can become a higher potential in negentropy than incineration in practice, they should be proposed to substitute incineration in the future. Back to a state-of-the art in both research and engineering, low-grade thermal energy can be transformed into high-grade heat for electricity generation via drying and incineration, reaching the maximal exploitation of chemical energy. Last but not least, the hazardous air pollutants (e.g., NO_x, SO_2, heavy metals and PCDDs/PCDFs) produced in incinerated sewage sludge ash (ISSA) can be effectively controlled through staged air combustion, Ca-based additive, Cl-base additive and N-containing compounds, respectively (Liang et al., 2021). After incineration, most phosphate from the inflow (up to 90%) accumulates in ISSA (about 8% dry weight) which is comparable to that of low-grade phosphate rocks, and can be fully recovered more easily than by other approaches (Fahimi et al., 2021; Hao et al., 2013; Ma and Rosen, 2021). For this reason, it has become a consensus on recovering phosphorus from ISSA (Egle et al., 2016). Moreover, P-recovery from ISSA has a high efficiency up to 95%, which can substitute the conventional production of monocalcium phosphate to improve the performance on LCA (Faragò et al., 2021); some LCA results revealed that the AshDec® process, the acidic wet-chemical leaching process LEACHPHOS® and also direct integration into the fertilizer industry with wet-chemical extraction all indicated only a low change in cumulative energy demand as the additional demand for chemicals and energy can be offset by the P-fertilizer credits (Amann et al., 2018). Moreover, heavy metals removed from P-recovery have also a potential to be recovered with some applied technologies, such as wet chemical phosphorus recovery (Liang et al., 2019; Petzet et al., 2012), Fe and Al recovery for producing coagulants by Phos4life® (Morf et al., 2019) and Ash2®Phos (Cohen et al., 2018). Based on the P-recovery technology catalog of European Sustainable Phosphorus Platform (ESPP) (ESPP, 2019), there have been already some full-scale plants of P- and metals-recovery from ISSA in Europe, and EasyMining's Ash2Phos technology with the high recovery efficiencies on P, Al, and Fe (90–95%, 60–80% and 10–20%, respectively) has been applied in a plant in Helsingborg, Sweden, which has a low energy consumption and a favorable mass balance. Anyway, recovering phosphorus and metals from ISSA are being practiced in Europe, especially in the Netherlands, Switzerland and Germany. Finally, the remaining ash after the recovery of phosphate and heavy metals can be utilized in building materials. Comprehensive utilization of thermal energy and sludge resources would reduce entropy production and enhance negentropy, creating an ideal approach to SWWT.

In summary, the changes caused by modern civilization, beginning in and based upon the Industrial Revolution, have had the effect of making human civilization deviate from the natural entropy cycle. Natural purification is becoming less effective, and it has become necessary to treat wastewater and to develop and apply CWWT. As a result, entropy production has become an undoubtedly real phenomenon (as shown by the red curve in Fig. 1b). Under these circumstances, developing SWWT that emphasizes resource and energy recovery must be our top priority in order to delay entropy production and/or accelerate negentropy.

5. Conclusions

Based on the above discussion and analysis, some conclusions can be drawn, as follows:

- Water self-purification can help preserve the natural cycle of entropy, but is becoming less available now as more and more wastewater is being produced and water self-purification capacity becomes increasingly limited in an urbanized world.
- Wastewater can cause entropy production in the environment, and conventional wastewater treatment (CWWT) can even intensify the process of entropy production.
- It is necessary to develop sustainable wastewater treatment (SWWT) capable of reducing entropy production and accelerating negentropy. Among others, resource and energy recovery during wastewater treatment can help negentropy.
- Organics in wastewater should be recycled between high value-added organic chemicals, instead of being converted into CH_4. Thermal energy contained in the effluent should be fully utilized to realize carbon-neutral operation and even "carbon sink" of wastewater treatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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