

"Cycle closure" in waste management: tools, procedures and examples

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Abstract

Green Chemistry is a philosophy of chemical research and application that encourages the design of appropriate products/processes in order to minimize the use and production of hazardous chemicals. Green Chemistry involves the application of new, milder synthetic pathways, the avoidance of toxic solvents' use, the use of alternative sources of raw materials, the prevention of pollution, the design of environmental friendly products, the protection of workers' health and the reduction of energy consumption.

Wastewater treatment plants consume significant amounts of energy for collection, transport, processing and final disposal of water and by-products. Attempting to reduce the respective energy costs, energy recovery is an attractive alternative, as liquid wastes considered to contain significant amounts of energy. In addition, many technologies have been developed recently to recover useful materials from liquid wastes (phosphorus is a typical example).

In 2012, the EU-28 Member States discarded 2.5 billion ton of wastes, of which 4% was classified as hazardous, hence immediate and environmental friendly solutions are requested. The need to record and report the Environmental Footprint of an enterprise/industry becomes imperative. The adoption of green practices can act as catalyst to improve the processes of an enterprise, to reduce the cost of products and to maintain an environmental responsible attitude.

Keywords: Circular economy, combined heat and power system (CHP), ecological footprint, energy saving, green chemistry, materials recovery, phosphorus recovery, waste management.

1. Introduction

Green Chemistry is a philosophy of chemical research and practical application (technology) that encourages the design of appropriate products and processes in order to minimize the use and production of hazardous chemicals. For this reason, Green Chemistry includes the application of new, milder chemical synthetic compounds, the avoidance of the use of toxic solvents, the use of alternative sources of raw materials, the prevention of pollution, the design of environmentally friendly products, the protection of health of workers and the reduction of energy consumption. The main purpose of Green Chemistry is to promote sustainable development (Zouboulis, 2015).

However, in order to ensure sustainable development, the available natural resources should be used in a smarter, more efficient and more sustainable way. The linear economic growth model, on which was based in the past the development of the economy, is no longer considered as appropriate to meet current needs and is now being replaced by the circular economy model. According to this model, the value of products and materials should be maintained for as long as possible, the waste generated and the use of natural resources minimized, while the used resources are kept within the economy until a product has reached the end of its useful life cycle, and then can be reused, in order to create further value (Figure 1) (http://www.titan.gr).

The shift from the original linear model "take, make, consume, dispose" to the circular economy model, which gives emphasis on "reduce, reuse, repair, recycle, recover" requires changes from initial product design to consumption. The circular economy promotes the closure of individual cycles, making better use of energy and creating smart and reliable products. It leads to maintaining and enhancing physical capital, optimizing the use of natural resources, and shielding against negative external economic developments. It is estimated that the circular economy by promoting self-sufficiency in raw materials could generate over \$ 1,000 billion of annual material savings worldwide by 2025, through the implementation of new business models (Figure 2) (https://www.accenture.com/us-en/insight-circular-advan tage-innovative-business-models-value-growth).

The circular economy is based on a number of key principles, the main ones of which are presented below:

- Product design for re-use,
- Strengthening the durability of products,
- Exploitation of energy from renewable sources,

- Adoption of system approach and appropriate models,
- Developing common values.

The fact that the European Commission today places a particular priority on adopting the principles of the circular economy is particularly optimistic. This, at least, demonstrates the ambitious framework set by the European Union at the end of 2015, which is designed to address the major wounds of the modern economy, such as saving resources, boosting competitiveness, creating jobs and promoting growth. If the European Union becomes more resource-efficient managing natural resources and reducing its dependence on non-renewable raw materials, will be able to develop a serious competitive advantage by reinforcing its position in the global environment (Hellenic Association of Young Entrepreneurs, 2016).



Figure 1. Circular economy philosophy (http://www.titan.gr)

2. Energy and materials recovery from wastewater

A typical example of reflection, understanding and application of the nascent thinking of the circular economy constitutes wastewater treatment plants. Wastewater treatment plants consume significant amounts of energy for wastewater collection, transport, processing and final disposal. In recent years, the energy requirements of these plants have been rising as population growth has led to their expansion, while the ever-stricter permissible discharge limits for the various pollutants require prolonged wastewater treatment. These factors, coupled with the fact that energy costs are constantly increasing, have greatly increased the operating costs of processing plants. In addition, the potential exhaustion of fossil fuels promotes the need for maintaining and properly managing the energy in a processing plant. In order to reduce energy costs, energy recovery is an attractive alternative, as the wastewater contains a lot of energy content.

The usual method of recovering energy from liquid waste is the anaerobic digestion of the bio-solid (bio-sludge) produced by biological wastewater treatment to produce biogas, which is considered as a renewable energy source (RES). The bio-sludge contains particles that have been removed from the waste and have high organic matter and other nutrients concentration. The sludge, after increase in its concentration, is passed to a heated digestion tank. The digester operates under oxygen deficient conditions and in a slightly alkaline pH (pH \approx 8). Anaerobic bacteria under these conditions could convert organic matter to biogas in a four-step process (hydrolysis, oxidation, acetogenesis, methanogenesis), usually in two temperature ranges, which are 25-45 °C (mesophilic), or 55-60 °C (thermophilic). Biogas consists mainly of a mixture of methane (50-75%), carbon dioxide (25-45%) and other components, such as moisture and hydrogen sulfide (2000-3000 mg/L), traces. The production of biogas during anaerobic digestion is influenced by many factors, such as the solid concentration of sludge, the organic matter biodegradability, the treatment time and the digester temperature, e.g. by increasing the concentration of sludge solids, the amount of biogas produced is increased.



Figure 2. New business models for circular economy (https://www.accenture.com/us-en/insight-circular-advantageinnovative-business-models-value-growth)

A typical way of saving energy in wastewater treatment plants is to exploit the produced biogas. Biogas is a valuable of energy with a calorific value source of 20-25 MJ/m³ or 6,5 kWh/m³, which corresponds to about 60% of the natural gas's calorific value. Biogas can be used for heat and electricity production, and after being processed and properly upgraded, it can be used either as "biofuel" or fed into the natural gas network. Its use as biofuel is already being implemented in Switzerland, France, Sweden and Germany, while in the latter two countries is also being used in the grid. However, carbon dioxide, humidity, hydrogen sulphide, as well as other trace minerals should be removed to a sufficient concentration before use, in order to obtain a relatively stable calorific value and prevent problems in the recovery equipment corrosion). The produced biogas can be used on site in the wastewater treatment plant in direct-combustion systems, such as boilers. In boilers, biogas burns in the combustion chamber and the produced heats could be used for the water (or other liquid) flowing into the pipes heating. Heat converts water to steam and through the pipes steam transfers the heat to the points of consumption. This

energy can be used for space heating in sewage treatment plants, or for heating processes of the same installation and/or other industries (industrial immersion). For example, the heat produced by the combustion of biogas could be used to preheat sludge fed to the digester, sludge drying, and/or incineration. The quality upgrade of biogas is not required when it is used to produce heat in the plant. However, it is necessary to remove some undesirable components, such as moisture and hydrogen sulfide, in order to prevent from erosion, mechanical equipment degradation, as well as the emission of toxic gases. Biogas combustion produces SO₂/SO₃ which are much more toxic than H₂S, while the accumulation of water in the biogas production line contributes to the formation of H₂SO₃ which is a highly corrosive component. Concentration of H₂S up to 1000 mg/L is generally permissible for the use of biogas in these special combustion boilers.

Apart from the previous application of biogas, a different method of its utilization is in Combined Heat and Power (CHP) systems (Figure 3) (Haefke, 2009; Kapreli, 2011; Berger, 2013; Hugh Monteith, 2011). These units include the simultaneous generation of electricity and heat from a fuel source, such as biogas. CHP plants have biogas quality requirements similar to boilers, with the substantial difference that the H_2S concentration should be even lower. A typical CHP unit includes a motor, an electric generator, a heat recovery system and an evaporator. The internal combustion engine exploits biogas to drive the generator and thus generates electricity. Heat is recovered either through the engine cooling circuits or through the flue gas.

CHP plants are considered a very efficient method of using biogas for energy production. These systems achieve fuel conversion efficiencies of up to 90%. Electricity generation ranges between 20-35%, while heat output ranges between 50-65%. Modern systems achieve electricity yields of up to 48%. The rest is energy losses. In addition, CHP systems offer significant environmental benefits compared to conventional power generation systems. By collecting and utilizing heat, which would otherwise be unused, in the production of electricity, fuel consumption is reduced to produce the same amount of energy. Since fewer fuels are needed, greenhouse gas emissions, such as carbon dioxide (CO_2) and other air pollutants such as NOx and SO_2 are significantly reduced (Figure 4) (https://www.epa.gov/chp).

The electricity generated by CHP plants can be used on site to meet the energy needs of the plant. Biogas electricity produced can be used to operate electrical equipment such as pumps, control systems and agitators. In addition, part of the electricity can be sold to the electricity network. The heat generated by the CHP units can be used to heat rooms and processes (reheated heating, heating the sludge entering the digester) of the plant and also for the supply of hot water. An alternative use of the energy produced is the provision of heat and hot water in the local area. Heat reaches consumers through a pipeline network. The pipes must be well insulated and installed beneath the ground to minimize energy losses. Another alternative use of biogas is to channel it into the natural gas network, or to use it as a complementary biofuel.



Figure 3. A typical combined heat and power (CHP) system (Haefke, 2009)



Figure 4. Emissions of conventional/CHP air pollutants (https://www.epa.gov/chp)

Moreover, urban and industrial waste liquids can be described as a renewable source of thermal energy as they have the following characteristics: huge amounts of waste are produced annually in cities whose temperature is lower than this of environment in the summer and higher in the winter, with slight fluctuations over time, and finally containing large amounts of thermal energy. These characteristics make the liquid waste an ideal case of recovering this energy through heat pumps. Usually this energy remains unspent as it is excreted in the environment. It is therefore very important to recover it as the heat generated can be used to heat the plant's premises, provide hot water, or other plant processes that require heating, such as anaerobic digestion and drying sludge, thereby reducing the overall energy requirements of the plant. In addition, this heat can be transferred to the district heating system to heat buildings and provide hot water.

The systems used to recover the heat contained in the liquid waste are either heat exchangers or heat pumps (Hepbasli, 2014; Chua, 2010; Hepbasli, 2009; Berger, 2013). In the first system the effluents flow into the exchanger

containing one more liquid than the sewage. The heat is transferred to the other liquid that has a lower temperature than that of the sewage. This type of system is placed in smaller scale applications. Larger systems include a heat pump that is much more efficient than heat exchangers and can increase recovery performance as it can also be used to cool rooms during the summer months.

In heat pump systems, the liquid used, which has lower temperature than the sewage, receives the heat from the liquid waste. The used liquid is led to a compressor, which increases the pressure and temperature of the liquid. Then, the compressed fluid is led to a condenser, where the heat is released, so that it can be used. After condenser, the cold liquid is led to an expansion valve where its pressure and temperature are reduced to an appropriate level, where the heat from the sewage can again be transferred to the liquid. One of the most important factors affecting the amount of recovered heat is the change in the temperature of the waste water. The higher the temperature drop from the system, the greater the amount of thermal energy can be recovered. In particular, reducing the temperature of waste water by 1 ° C can lead to a daily energy output of 700 MWh.

In recent years, special technologies have also begun to develop useful materials from liquid waste. A typical example is phosphorus (use in fertilizers), as its reserves are estimated to be exhausted within the next 50-100 years. From 1950 to 2000, phosphorus value rose 10 times, and only in 2007 its value rose by 200%. As a result, countries with a shortage of phosphoruscontaining minerals (including most of the European Union countries) are completely dependent on their import and are therefore vulnerable to these market fluctuations. During the biological treatment of the liquid waste, 90% of the removed phosphorus is concentrated to the active sludge, while the remaining 10% is precipitated and removed in the form of iron or aluminum chlorides, in order to avoid eutrophication problems from the disposal of treated waste water to water recipients. The produced sludge containing 1-5% P, and in some cases the concentration of P can reach up to 15% in the dry residue. The simplest method of recovering and using P is to directly use the sludge produced as fertilizer, provided that the appropriate terms and conditions for its incorporation are met. However, sludge may also contain significant amounts hazardous organic compounds (e.g. of aromatic hydrocarbons), but also heavy metals. Consequently, the regulations for the direct disposal of sludge are becoming ever more stringent and new methods of phosphorus recovery are being developed. Recovery techniques that have been developed can be applied at various points in the waste treatment (Egle, 2016; Zhou, 2017; Oleszkiewicz, 2015; Rodogianni, 2012; Raptopoulou, 2016; Kailatzidou, 2016). Phosphorus can be recovered from the liquid phase, from the produced sludge, but also from the carbonized sludge ashes.

In order to be economically viable the phosphorus recovery, the liquid phase concentration should be at least 50-60 mg/L of P. As the concentrations of P in the effluent

of urban waste water treatment plants are less than 5 mg/L, the parallel flows of anaerobic digestion or sludge dewatering process flows are more appropriate to make phosphorus recovery more efficient. These streams usually have phosphorus concentrations of 20-100 mg/L but also up to 300-900 mg/L, respectively. Sludge resulting from anaerobic digesters, either unprocessed or dehydrated, contains phosphorus at а concentration of 1-5% of its weight. In the case of carbonized sludge, the resulting ash has higher concentrations of phosphorus, ranging between 5-11%, in some cases reaching even 20%. At the same time, during the carbonization of the sludge, heavy metals are not modified (they are considered as a "preservative pollutant"), resulting in the need to their effective removal from the final product. The recovery rate of P from the liquid phase is between 40-50%, while from the sludge, or from the sludge ash, it can reach up to 90%. Figure 5 shows the possible phosphorus recovery sites in a wastewater treatment plant from the aqueous phase (1), the produced sludge (2) and the carbonized sludge ash (3).



Figure 5. Possible phosphorus recovery sites during wastewater treatment (Rodogianni, 2012)

3. Environmental footprint

In 2012, the 28 member states of the EU rejected 2.5 billion tons of waste. A percentage about 4% was classified as hazardous, therefore immediate solutions are needed to confront this problem in an environmental friendly manner. In this context, the need to record and the report environmental footprint of an enterprise/industry, both globally and at the level of processes and products, becomes imperative. The Ecological Footprint measures the ecological assets that a given population requires to produce the natural resources it consumes (including plant-based food and fiber products, livestock and fish products, timber and other forest products, space for urban infrastructure) and absorb its waste, especially carbon emissions. to The Ecological Footprint tracks the use of six categories of productive surface areas: cropland, grazing land, fishing grounds, built-up land, forest area, and carbon demand on land. Although there are many different types of environmental footprint (e.g. water, carbon, ecology, etc.), for reasons of brevity, the term "Environmental Footprint" often refers to carbon dioxide equivalents (eCO₂) emissions. Biocapacity is the productive area that can regenerate what people demand from nature. Footprint and biocapacity can be compared at the individual, regional, national or global scale. Both footprint and biocapacity change every year with number of people, per person consumption, efficiency of production, and productivity of ecosystems. At a global scale, footprint assessments show how big humanity's demand is compared to what planet Earth can renew.

Efforts to measure and reduce the Environmental Footprint through the adoption of appropriate green (environmental friendly) practices can act as a catalyst to improve the processes of a productive enterprise, reduce the cost of products, and maintain an environmentally responsible attitude towards the rest of the trade and social partners.





Carbon footprint measures the total amount of carbon dioxide emissions produced directly or indirectly by a human activity, or accumulated during the life stages of a product, commodity or service. The footprint takes into account all six main greenhouse gases as described in the Kyoto Protocol: Carbon dioxide (CO₂), Methane (CH₄), Nitrogen monoxide (N₂O), Hydrofluorocarbons (HFCs), and sulfur Perfluorocarbons) hexafluoride (SF_6) . Figures 6a and 6b show the carbon footprint for the various forms of energy production and the "intensity" of the used carbon to produce energy, according to the geographic area [20]. Thus, CO₂ emissions are minimal in the case of hydropower, wind and ocean energy, while taking its maximum value with the use of fossil fuels. The global average carbon footprint in 2007 was around 5.7 tons CO₂e/cap. The EU average for this time was about 13.8 tons CO₂e/cap, whereas for the U.S., Luxembourg and Australia it was over 25 tons CO₂e/cap. The footprints per capita of countries in Africa and India were well below average. Mobility (driving, flying & small amount from public transit), shelter (electricity, heating, construction) and food are the most important consumption categories determining the carbon footprint of a person. Indicatively, a simple e-mail adds about 4 gCO₂e to the atmosphere, which even if it has a large attached file, then the charge reaches 50 gCO₂e. A spam even if it does not open, it emits 0.3 gCO₂e while a text message from a mobile phone "emits" about 0.014 gCO₂e. The most common way to reduce the carbon footprint of humans is to Reduce, Reuse, Recycle, Refuse. In manufacturing this can be done by recycling the packing materials, by selling the obsolete inventory of one industry to the industry who is looking to buy unused items at lesser price to become competitive. Nothing should be disposed off into the soil, all the ferrous materials which are prone to degrade or oxidize with time should be sold as early as possible at reduced price.

Water Footprint is an alternative indicator of freshwater consumption, which takes into account both the direct and indirect water consumption of a user [21] and is defined as the total fresh water volume (m³) consumed by a person, or community to produce various products and services.

The water footprint has three components: green, blue and grey. Together, these components provide а comprehensive picture of water use by delineating the source of water consumed, either as rainfall/soil moisture or surface/groundwater, and the volume of fresh water required for assimilation of pollutants. Green water footprint is water from precipitation that is stored in the root zone of the soil and evaporated, transpired or incorporated by plants. It is particularly relevant for agricultural, horticultural and forestry products. Blue water footprint is water that has been sourced from surface or groundwater resources and is either evaporated, incorporated into a product or taken from one body of water and returned to another, or returned at a different time. Irrigated agriculture, industry and domestic water use can each have a blue water footprint. Grey water footprint is the amount of fresh water required to assimilate pollutants to meet specific water quality standards. The grey water footprint considers point-source pollution discharged to a freshwater resource directly through a pipe or indirectly through runoff or leaching from the soil, impervious surfaces, or other diffuse sources.

Figure 7 presents the global footprint in m³/inhabitant/year (Hoekstra, 2007). Generally, the world map of water footprint shows an image similar to greenhouse gas emission map, which shows that high water consumption keep up with energy demand, as a result of an existing energy and hydropower model. Particularly unfavorable is our country's position as regards water consumption. With an average annual consumption of 2.389 cubic meters per inhabitant, we have the second largest water footprint after US and twice the world average (1.243 cubic meters/year/inhabitant). Our high water footprint is attributed to the increased use of water for agriculture (85%), to the losses of the country's dated irrigation and water supply network, and to the overall mismanagement of water resources.

Four are the key factors determining the water footprint, according to Professor A.Y. Hoekstra, one of the main authors of this index. The primary factor is the amount of consumption and then the quality and composition of consumption. For example, a country that feeds a lot of meat spends more water to produce it. The third factor is the effect of climatic conditions, if required e.g. a large proportion of irrigation for crop growth, and the fourth is related to the way of production in the agricultural sector.

The assessing of a product water footprint could shape the possibilities for implementing new water management policies, since it involves more participants. Thus, while water resources have so far been mainly associated with water consumption for the irrigation of basic crops, final consumers, traders, food industries, etc. which have traditionally been outside the framework of water resource management interventions, are now emerging as watersaving factors that are used either directly or indirectly for the production of finished products. More specific options, such as the materials handling techniques at the various intermediate stages, the means of transport and the distances to be traveled, the distribution system and the supply chains in general, are the main decision variables of optimizing the water resources management with the aim of minimizing the final product water footprint.



Figure 7. The global map of water consumption (footprint) (Hoekstra, 2007)

4. Conclusions

The transition to a more circular economy, where the value of products, materials and resources remains in the economy as much as possible, and the waste generation is minimized, is a necessary contribution to European Union's efforts to develop a sustainable, competitive, low-carbon. Such a transition will be an opportunity to transform the European economy and Europe and gain new, sustainable and competitive advantages.

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