CHARACTERISTICS OF EFFLUENT ORGANIC MATTER IN WASTEWATER

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Contents

Summary

Wastewater reuse is being increasingly promoted as a strategy for conservation of limited resources of freshwater and as a mean of safeguarding the aquatic environment from contaminants present in wastewater. Although secondary and tertiary treated wastewater is often discharged into surface waters, it cannot be used for reuse purposes without further treatment. Some of the parameters of concern for human and environmental health are components of organic matter originating from wastewater treatment plant (WWTP) effluents. This effluent organic matter (EfOM) should be carefully characterized in order to find an optimum treatment method for water reuse. This review presents characteristics and analyses of EfOM components present in WWTP effluents.

1. Introduction

Wastewater treatment is employed as an action to protect the quality of limited freshwater resources and therefore make it more acceptable for beneficial reuse. However, achieving this objective remains elusive as the total discharge of biologically treated sewage effluent (BTSE) is continually on the rise due to increasing population and urbanization. Wastewater reclamation is recognized as one of the most effective ways of increasing the availability of limited freshwater and at the same time, the use of reclaimed water can reduce the demand for freshwater. For the purpose of wastewater reclamation/reuse, it is imperative to study the characteristics of effluent organic matter (EfOM) in the BTSE in detail in order to design effective treatment methods.

2. Overview of EfOM

The systematic treatment of wastewater was started in the late 1800s and early 1900s (Tchobanoglous and Burton, 1991). For the last two centuries, wastewater treatment has continually been developed to meet increasingly stricter disposal standards. Recently, wastewater for reuse is being increasingly emphasized as a strategy for conservation.

Although many previous researchers have worked extensively on natural organic matter (NOM) in surface waters, there have been few studies related to EfOM in wastewater. This is probably due to the diverse characteristics of wastewater which vary by place and season. However, as concerns related to water reuse increase an interest in characterizing the EfOM has become more important.

The composition of EfOM is a combination of those of NOM, soluble microbial products (SMPs) and trace harmful chemicals. Most of the NOM originates from drinking water, which is one of major components in wastewater, while SMPs come from biological treatment with the WWTP and non-biodegradable organic matter. Of particular interest are recalcitrant organic chemicals which are resistant to biodegradation, and thus challenging to remove during typical wastewater treatment. Some micro-contaminants associated with wastewater effluent may cause adverse impacts to aquatic and human health if the compounds are present in recycled water. Some of the compounds of concern include: disinfection by-products (DBP), *N*-nitrosodimethylamines (NDMA), pesticides, herbicides, pharmaceuticals and endocrine disrupting chemicals (EDCs) (Boyd et al., 2003; Kim et al., 2006).

3. Typical Processes Used in Wastewater Treatment

Wastewater collected from municipalities, communities and industries contains a wide range of pollutants. The treatment train normally adopted includes physical, chemical, and biological methods. WWTP is divided into four major treatment groups: i) preliminary, ii) primary, iii) secondary, and iv) tertiary advanced treatment. Conventional sewage treatment includes primary treatment to remove the majority of suspended solids, secondary biological treatment to degrade the biodegradable binding organic matter and nutrients and tertiary treatment to remove a portion of the remaining organic and inorganic solids and pathogenic microorganisms through a filtration step.

The preliminary treatment of wastewater removes coarse and readily settleable inorganic solids with the size range of more than 0.01 mm, such as sand and grit particles. The removal is carried out using screens and grit chambers, respectively. After coarse and floating solids are removed in preliminary treatment, primary treatment removes the bulk of suspended solids through sedimentation tanks or clarifiers. During sedimentation, particles from 0.1 mm to 35 μm including both organic and inorganic matter are removed. Of the 70-90 percent of suspended solid removed by sedimentation, 30-40 percent of this reduction is oxygen-demanding suspended solids (Tchobanoglous and Burton, 1991).

Secondary treatment is employed to remove oxygen-demanding organic pollutants which are present mostly in the dissolved form. This process utilizes bacterial biological degradation to remove the dissolved pollutants. However, these microbes will produce SMPs and extracellular polymeric substances (EPSs), which can be toxic and inhibit nitrification.

Tertiary treatment removes part of the remaining organic pollutants through a filtration process. Final disinfection is often utilized to reduce the bacterial count, particularly pathogenic microbes. This is mainly adopted to avoid poorly treated effluent quality and to protect the receiving water.

4. Wastewater Characteristics

An understanding of the chemical composition of wastewater is important since this allows an understanding of reactions and interactions with the organic and inorganic compounds (Roila et al., 1994). The organic and biological composition of wastewater is a reflection of the influent water usage (such as industrial, domestic and agricultural activities). Wastewater is treated, discharged to a receiving stream, and withdrawn for reuse by a downstream population. Consequently, the chemical and bacteriological composition must be monitored to ensure public health.

Concentrations of nutrients, such as nitrogen and phosphorus, should be reduced to a level protective of the receiving stream (e.g., eutrophication and subsequent siltation). Releases of microbiological contaminants and other pollutants should also be minimized to protect downstream users. The organic composition of wastewater is approximately 50 percent proteins, 40 percent carbohydrates, 10 percent fats and oils, and trace amounts (e.g. μg/L or less) of priority pollutants, surfactants, and emerging contaminants. The microbiological composition of domestic wastewater often contains 10^5-10^8 colony forming unit (CFU)/mL of coliform organisms, 10^3-10^4 CFU/mL fecal streptococci, 10^1-10^3 protozoan cysts, and 10^1-10^2 virus particles. For adequate protection of public health, the safety of wastewater discharged to a receiving stream must be ensured (Ellis, 2004).

Fundamental information on specific characteristics of organic matter is important in the optimization of treatment processes used in WWTP. The chemical composition of the sediments, organic macromolecules, or sewage sludge has been identified in many studies (del Rio et al., 1998; Réveillé et al., 2003; Müller et al., 2000; Her et al., 2002; Leenheer and Croue, 2003).

5. Constituents of EfOM in BTSE

The presence of trace organic pollutants in wastewater has been the cause of increasing public concern in recent decades due to potential health risks. EfOM in wastewater consists of both particulates and dissolved substances, which has been found to include several trace organic contaminants including EDCs and PPCPs (Halling-Sorensen et al., 1998; Daughton and Ternes, 1999; Snyder et al., 1999; Snyder et al., 2001d; Vanderford et al., 2003). EfOM can be summarized into three general classes based on their origins:

(i) NOM derived from drinking water sources,
(ii) Synthetic organic compounds produced during domestic use and disinfection by-products generated during disinfection processes of water and wastewater treatment and
(iii) SMPs derived during biological processes of wastewater treatment (Drewes and Fox, 1999).

The constituents that are found in BTSE are shown in Table 1, (Levine et al., 1985). The fraction of particulate organic material measured as suspended solids (SS) includes protozoa, algae, bacterial floc and single cell, microbial waste products and other miscellaneous debris. Dissolved organic matter (smaller than 0.45 µm) are typically cell fragments and macromolecules. Thus, EfOM can be classified into two main groups by size groupings:

(i) Particulate organic carbon (POC) above 0.45 µm and
(ii) Dissolved organic carbon (DOC) below that limit. Both groups include a wide variety of constituents (Table 1).

Organic constituents in BTSE	**Size (µm)**	**Molecular Weight (daltons)**
Particulate organic carbon (POC)		
Bacteria	$10\text{-}10^{1}$	
Organic Debris	$10\text{-}10^{3}$	
Algae and protozoa	$10\text{-}10^{3}$	
Dissolved organic carbon (DOC)		
Recalcitrant matter		$5\text{x}10^{1}\text{-}10^{3}$
Humic acid		$10^{3}\text{-}10^{6}$
Nutrient		$10\text{-}10^{2}$
RNA		$10^{4}\text{-}10^{7}$
Cell fragment		$10^{7}\text{-}10^{9}$
Chlorophyll		$5\text{x}10^{2}\text{-}10^{4}$
Polysaccharide		$10^{4}\text{-}10^{7}$
Carbohydrate		$10^{2}\text{-}10^{3}$
Protein		$10^{4}\text{-}5\text{x}10^{8}$
Amino acid Vitamin		$5\text{x}10^{1}\text{-}5\text{x}10^{2}$
Vitamin		$10^{3}\text{-}10^{4}$
Virus		$10^{6}\text{-}10^{9}$
Fatty acid		$10^{2}\text{-}10^{3}$
Extracellular enzyme		$10^{4}\text{-}10^{5}$
DNA		$10^{8}\text{-}10^{9}$

Table 1 Typical organic constituents in BTSE and their size ranges

Painter (1973) and Levine et al. (1985) showed that organic contaminants of interest in wastewater range in size from less than 0.001 µm to well over 100 µm. The major macromolecules in BTSE are the polysaccharides, proteins, lipids, nucleic acids and NOM (Levine et al., 1985). EfOM in the range from 10^{3} to 10^{6} Da include humic acids and fulvic acids present in drinking water. Wastewater compounds smaller than 10^{3} Da include carbohydrates, amino acids, vitamins, and chlorophyll. Persistent chemical compounds such as dichloro-diphenyl-trichloroethane (DDT), polychlorinated biphenyls and other substances of public health are often lower molecular weight (MW) compounds (Stull et al., 1996; Pempkowiak and Obarska-Pempkowiak, 2002). To remove these compounds, it is important to examine the interrelationship between the ranges of contaminant size and wastewater treatment operations and processes.

The POC includes zooplankton, algae, bacteria, and debris organic matter from soil and plants. It can easily be removed by solid-liquid separation processes. However, the DOC can pass on many effects on water quality and therefore it remains a focus of research in wastewater treatment (Shon et al., 2005a). Figure 1 shows the most significant DOC components in water in terms of different fractions, (Thurman, 1985; Cho, 1998).

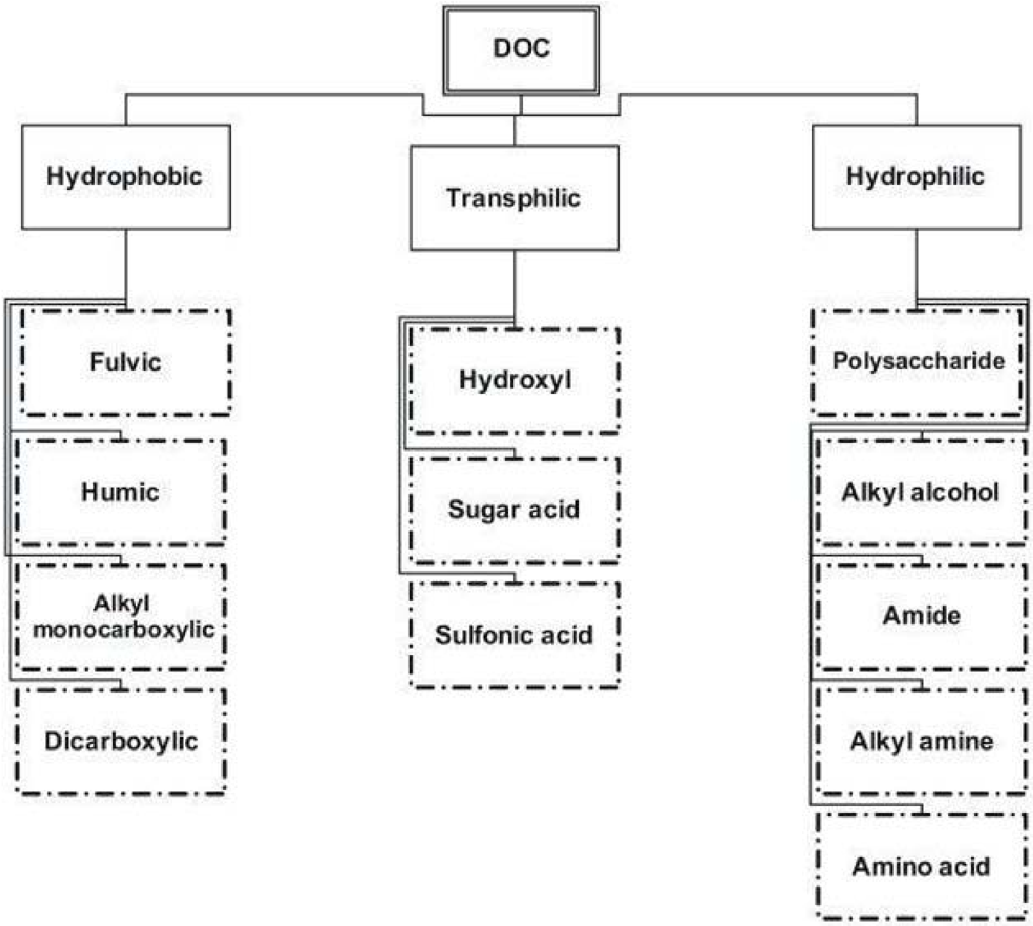

Figure 1 Different fractions of DOC and their constituents.

6. Adverse and Benign Effects of EfOM

EfOM affects essentially all chemicals and biological processes in aquatic environments. It has a stabilizing effect, opposite to that of metal ions. EfOM can have the following consequences:

(i) Precursor for the formation of disinfection-by-products,
(ii) Exerts higher coagulant and oxidant demands,
(iii) Fouls adsorbents and membranes;
(iv) Causes corrosion problems, and
(v) Supplies substrate for biomass growth in water distribution networks.

The presence of EfOM in BTSE can also be helpful in some instances. For instance, EfOM substances can bind with metals and organic compounds to reduce bioavailability and subsequent toxicity. Some treatment processes implicitly benefit from the physico-chemical effects of EfOM on colloids. Humic acids can be used as direct means to extract pollutants (Yates and Von Wandruszka, 1999).

7. Characteristics of EfOM from BTSE

Wastewater qualities can be classified into 3 groups: i) physical, ii) chemical and iii) biological. The physical characteristics include color, odor, solids and temperature; chemical characteristics include the amount or concentration of carbohydrates, fats, oils and grease, pesticides, phenols, proteins, surfactants and volatile organic matter, alkalinity and chlorides, heavy metals, nitrogen, phosphorus, sulfur, hydrogen sulfide and methane, oxygen; and chemical characteristics include animals and plants, eubacteria and archaebacteria, viruses. The sources of these various characteristics are outlined in Tchobanoglous and Burton (1991). It should be noted that many of the parameters listed are interrelated. Tchobanoglous and Burton (1991) observed that temperature, a physical property, affects both the biological activity in the wastewater and the amounts of gases dissolved in wastewater.

Conventional wastewater treatment cannot remove all contaminants, as recent discoveries have indicated that trace chemicals in effluents can impact fish at ng/L concentrations (Bevans et al., 1996; Kramer et al., 1998; Renner, 1998; Jobling et al., 2003; Snyder et al., 2004a; Parrott and Blunt, 2005). Suspended solids can lead to developing sludge deposits and anaerobic conditions when unfiltered wastewater is discharged into an aquatic environment. In addition, their biological stabilization can lead to the depletion of oxygen and to an increase in septic conditions. Nutrients, particularly nitrogen, phosphorus, and carbon, are essential components for bacterial growth. When discharged into the aquatic environment, these nutrients can ultimately lead to the growth of undesirable aquatic life. However, nutrients are also essential for a healthy aquatic environment and some level of productivity is required to sustain healthy fish populations. Therefore, almost complete elimination of nutrients and carbon may have an unhealthy impact on receiving waters, hence careful thought should be given to any water quality changes in effluents discharged to surface water.

8. Analytical Methods of EfOM

Over the years, a number of different analytical methods have been developed to determine the organic content in waste waters. In general, these methods may be divided into those used to measure gross concentrations of EfOM greater than about 1 mg/L and those used to measure trace concentrations in the range of nano- and micro- sizes (Tchobanoglous and Burton, 1991). Here, EfOM includes both NOM and EfOM and the analytical method to measure NOM is the same as EfOM.

The organic pollutants are generally measured in terms of surrogate parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), etc. However, considering the harmful effects of trace EfOM such as DBP, EDC, PPCP, etc., they are also measured. The characterization of EfOM can also be classified into two groups of traditional analyses and numerous analytical methods (Her, 2002). Most chemical or physical characterization has been conducted on traditional analyses (e.g., light absorptivity, DOC concentration, aromaticity, fluorescence, XAD fractionation and MW) due to the difficulty and higher cost of detailed structure analysis. The advanced numerous analytical approaches include NMR, pyrolysis-GC/MS, IR, size exclusion chromatography (SEC) coupled to electrospray ionization quadrupole time-of-flight mass spectrometry (ESI-Z-TOF-MS) and thermogravimetric methods. The SEC coupled with ESI-Z-TOF-MS allows a better understanding of the chemistry of EfOM, of its complexing properties towards heavy metals and radionuclides for environmental studies (Plancque et al., 2001; Reemtsma and These, 2005). The most popular analytical methods of the characterization of EfOM can be defined as i) aromaticity by UV absorbance, charge density by potentiometric titrations, ii) hydrophobicity by fractionation, iii) functional groups by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), iv) polysaccharide, protein, lipid, and fatty acid by flash pyrolysis/gas chromatography/mass spectrometry analysis (pyrolysis/GC/MS), and v) molecular weight distribution (MWD) by high performance size exclusion chromatography (HPSEC).

In this chapter, EfOM is divided into specific EfOM components and aggregate EfOM. Detailed characteristics of EfOM by the classification will be presented in terms of origin, concentration, analytical method and effect.

9. Specific EfOM Components Present in BTSE

The contaminants in BTSE can be separated into size fractions based upon successive sedimentation, centrifugation and filtration. The four molecular size fractions are classified by range as settleable, supracolloidal, colloidal and soluble. The size range are less than 0.08 µm, 0.08 – 1.0 µm, 1 - 100 µm, greater 100 µm for soluble, colloidal, supracolloidal, settleable resecptively (Levine et al., 1985). The organic content varies with the amount of grease, protein, carbohydrates. For soluble organics is 12%, 4%, 58% of grease, protein, carbohydrates respectively (Levine et al., 1985).. An important conclusion from the early studies is that particles smaller than 1.0 µm can be degraded biochemically at a much more rapid rate than particles larger than 1.0 µm (Levine et al., 1985). Most of the EfOM in the treated water are found in the soluble fraction (86% of the COD). The elimination of EfOM by biological treatment is 90% for the soluble fraction and 96% for the bulk EfOM (Dignac et al., 2000). In a wastewater, approximate 75 percent of the suspended solids and 40 percent of the filterable solids are organic in nature (Levine et al., 1985). These solids are derived from both animals and plants as well as their activities. Organic compounds are normally comprised of a combination of carbon, hydrogen and oxygen with nitrogen in some cases. Other important elements, such as sulphur, phosphorus and iron, may also be present. Small quantities of a large number of different synthetic organic molecules include surfactants, organic priority pollutants, volatile organic compounds and agricultural pesticides. The number of such compounds is growing as organic molecules are continually being synthesized. The presence of these substances has complicated wastewater treatment because many of them either cannot be or are slowly decomposed biologically. Along with protein, carbohydrate, fat, oil, grease and urea, wastewater also contains small quantities of a large number of different synthetic organic molecules. Typical examples include surfactants, priority pollutants, volatile organic compounds, and agricultural pesticides. The presence of these substances has complicated wastewater treatment since several have been found to be resistant to biodegradation (Snyder et al., 2004b).

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Dr J. Cho, associate professor at Gwangju Institute of Science and Technology, has been studying on research for water reuse using various technologies, including constructed wetland and membrane filtration. He is recently interested in research of ecological engineering as well as related education. He is an editorial board member of Journal, Water Science and Technology, IWA and newsletter editor of Water Reuse Specialty Group in IWA.

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