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Review

A critical review on characterization strategies of organic matter for wastewater and water treatment processes

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HIGHLIGHTS

- Hydrophilic and neutral fractions of organic matter are the most significant foulants.
- Hydrophobic acids showed higher THMs formation reactivity than hydrophilic fractions.
- Humic substances were efficiently broken-down by ozone or Fenton reactions.
- Low molecular weight acids are not effectively removed by ozone.

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ABSTRACT

The presence of organic matter (OM) in raw wastewater, treated wastewater effluents, and natural water samples has been known to cause many problems in wastewater treatment and water reclamation processes, such as treatability, membrane fouling, and the formation of potentially toxic by-products during wastewater treatment. This paper summarizes the current knowledge on the methods for characterization and quantification of OM in water samples in relation to wastewater and water treatment processes including: (i) characterization based on the biodegradability; (ii) characterization based on particle size distribution; (iii) fractionation based on the hydrophilic/hydrophobic properties; (iv) characterization based on the molecular weight (MW) size distribution; and (v) characterization based on fluorescence excitation emission matrix. In addition, the advantages, disadvantages and applications of these methods are discussed in detail. The establishment of correlations among biodegradability, hydrophobic/hydrophilic fractions, MW size distribution of OM, membrane fouling and formation of toxic by-products potential is highly recommended for further studies.

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1. Introduction

Many countries all over the world are currently facing severe freshwater resource shortages due to increasing population, rapid economic growth, and extreme weather events brought on by climate change. In particular, the scarcity of fresh water is a critical problem that causes great concern in countries where natural water resources are limited. For this reason, wastewater reclamation plays an important role in developing strategies for water resource management worldwide. To date, the reuse of treated wastewater effluents from wastewater reclamation plants (WRPs) is considered to be an alternative water resource to

overcome the shortage of fresh water resources. However, the use of reclaimed water from treated wastewater effluents can pose potential health effects associated with microbial pathogens, heavy metals, pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), and other recalcitrant organic compounds, as secondary effluents are considered a major source of these contaminants (Luo et al., 2014; Tran et al., 2014a,b). The acceptability of reclaimed water for a given water reuse is dependent on the physical, chemical, and microbiological quality of the water. Up to now, there has been widespread agreement that a desirable treated wastewater effluent for the water reuse purpose is always required to be not only low in concentrations of organic and inorganic pollutants, but also free from biological entities, such as, faecal bacteria, enteric viruses and other emerging pathogens. It is therefore necessary to design, control, and operate a wastewater

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Nomenclatures

ASMs	activated sludge models	OND	organic nitrogen detection
AOPs	advanced oxidation processes	X_p	particulate inert microbial products
BOD	biochemical oxygen demand	S_H	rapidly hydrolysable fraction
bCOD	biodegradable COD	RO	reverse osmosis
COD	chemical oxygen demand	SEC	size exclusion chromatography
CAS	conventional activated sludge	S_p	soluble microbial products
DBPs	disinfection byproducts	SMPs	soluble microbial products
DOM	dissolved organic matter	K_S	the half-velocity constant
ECPs	extracellular polymers	$\mu_{H,max}$	the maximum specific growth rate
GAC	granular activated carbon	X_i	the particulate inert fraction
Y_H	heterotrophic biomass yield coefficient	S_S	the readily biodegradable fraction
HPLC	high performance liquid chromatography	X_S	the slowly biodegradable fraction
HiA	hydrophilic acids	S_i	the soluble inert fraction
HiB	hydrophilic bases	C_S	the total biodegradable COD
HiN	hydrophilic neutrals	C_T	the total COD
HoA	hydrophobic acids	C_i	the total inert COD
HoB	hydrophobic bases	X_T	the total particulate COD
HPI	hydrophilic fraction	S_T	the total soluble COD
HPO	hydrophobic fraction	TOC	total organic carbon
HoN	hydrophobic neutrals	TPI	transphilic fraction
MBRs	membrane bioreactors	UF	ultra-filtration
MW	molecular weight	UVD	ultraviolet detection at 254 nm
OCD	organic carbon detection	X_H	viable heterotrophic biomass

reclamation system capable of efficiently removing undesirable pollutants from wastewater cost-effectively that plays a key role in facilitating further water reuse applications. In the past, conventional activated sludge processes (CAS) which involve the natural biodegradation of pollutants by heterotrophic and autotrophic bacteria, such as nitrifying bacteria in the activated sludge in aerated bioreactors, are regularly employed to treat municipal/industrial wastewaters. However, the use of CAS for wastewater reclamation usually shows some drawbacks due to the difficulties in separating the suspended solids (SS) and low removal efficiency for many inorganic/organic pollutants. Subsequently, the treated wastewater effluents from CAS are limited for further water reuse applications. In recent decades, the combination of biological treatment with microfiltration (MF) or ultra-filtration (UF) has been considered as an attractive technology for industrial and municipal wastewater reclamation due to its high removal efficiency of pollutants and cost effectiveness. For instance, it is well acknowledged that the submerged membrane bioreactor (sMBR) shows better technical feasibility for the reclamation and reuse of municipal wastewater compared to CAS.

In reality, membrane technology, such as MF, UF, reverse osmosis (RO), and nano-filtration (NF), always provides a high degree of treatment in terms of SS, turbidity, faecal coliform, nitrogen, phosphorus and organic removal (Shon et al., 2004, 2006). However, it is evident that a major drawback of membrane-based treatment technologies is the membrane fouling that is caused by DOM fractions in raw wastewater/treated wastewater effluents. The membrane fouling affects the membrane performance, such as permeability and the OM rejection (Shon et al., 2006). Earlier studies reported that the humic substances (HS) fraction of OM is a major foulant, which controls the rate and extent of fouling, while recent studies have claimed that hydrophilic and neutral fractions of OM might be the most significant foulants (Tang et al., 2010; Lamsal et al., 2012). Thus, a good characterization of OM in wastewater samples can help optimize the performance of membrane filtration of biologically treated wastewater effluents through using appropriate pre-treatment processes, such as

flocculation with $FeCl_3$ and adsorption with powder activated carbon (Shon et al., 2004).

In addition to membrane technologies, the applications of advanced oxidation processes (AOPs), such as catalytic ozonation (He et al., 2013), Fenton/photo-Fenton oxidation (Nousheen et al., 2014), and photocatalytic oxidation involving UV/H_2O_2 (Shon et al., 2007; González et al., 2013) have been recognized as high potential technologies for wastewater reclamation and water reuse. However, AOPs are normally used to partially oxidize non-biodegradable OM with high molecular weight or recalcitrant OM to more biodegradable compounds due to the large consumption of energy and chemicals for complete oxidation and mineralization. The efficiency of AOPs in wastewater reclamation is influenced not only by the concentrations of OM but also by its physicochemical properties and molecular weight (Selcuk et al., 2006; González et al., 2013; Molnar et al., 2013). More recently, it has been demonstrated that the formation processes of disinfection by-products (DBPs) during chlorination and chloramination of secondary effluent for the production of high quality recycled water is affected by both the concentrations of DOM and DOM characteristics (Zhuo et al., 2001; Zhang et al., 2009; Doederer et al., 2014; Ma et al., 2014).

Apparently, the design, control, and operation of a wastewater reclamation system is largely dependent on how much is known about the characteristics of influent streams, the complexity of wastewater, and the degree of treatment required to meet the applicable discharge limits or reuse requirements. The design and operation of a wastewater reclamation system are reliable and effective only when the main components of wastewater are well characterized, particularly with regards to the characteristics of OM. However, the fact is that wastewater and reclaimed waters are complex and may contain a broad spectrum of both inorganic and organic pollutants that could affect the treatability. It is therefore necessary to choose suitable methods for characterizing OM in wastewater or reclaimed water samples for purposes of wastewater reclamation and further water reuse applications. This review summarizes the current knowledge on the characterization of OM in wastewater and reclaimed water. In addition, the advantages and disadvantages of characterization methods of OM are also discussed.

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