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Giusy Lofrano
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Green Technologies for Wastewater Treatment

Energy Recovery and Emerging
Compounds Removal

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Foreword

At a time when the world's population has reached seven billion people, sustainable design and environmental protection are critical to ensuring that water resources will be available for future generations. It is well recognized that there is an energy/water nexus. It takes water to generate energy and energy to treat water. There is great opportunity to make wastewater treatment plants net energy users and even producers since there is 2–4 times the amount of energy embedded in wastewater than it takes to treat it. As we design wastewater treatment plants, it is important to consider the kinds of treatment that will allow us to recover energy. It is also important to recover nutrients for use as fertilizers and to reclaim water for irrigation, since there is also a water/food nexus. Technology exists which allows wastewater to be treated to a level which removes micro-contaminants such as endocrine disruptors and pharmaceuticals which not only impact receiving waters and their uses, but also limits the ability for direct and indirect water reuse to ensure adequate supply of water. The editor, my friend and colleague Dr. Giusy Lofrano, in the framework of this book not only discusses the problems and issues associated with wastewater treatment but offers technologically sound solutions. This book is an asset to all water professionals so they can become knowledgeable in the issues and develop sustainable design for wastewater treatment plants.

Jeanette A. Brown

Preface

For as long as history has been recorded man has polluted and overexploited the environment in the pursuit of his own well-being. However, as everyone knows, nature itself is a source of pollution (volcanic eruption, natural burning, etc.)

Engineers occupy a strategic place in society because of their dualistic role. If on the one hand their work has sometimes a negative impact on the environment, on the other hand they help reducing or even eliminating pollution by developing treatment processes for water, solid waste and air.

According to the Royal Academy of Engineers, Engineering is “the application of scientific principles to the optimal conversion of natural resources into structures, machines, products, systems and processes for the benefit of humankind”.

Nowadays, it is well understood that we must make every possible effort to protect the environment. And now more than ever engineers must provide insights leading towards a sustainable standard of living to protect human and environmental health. However, although the concept of sustainable development has been defined more than 20 years ago, to date its application to actual technological context has not been so straightforward.

The main challenge that green engineering has had to face so far is the operational quest for sustainability. This means looking for strategies where water management and energy use are evaluated jointly. In order to meet this challenge, a number of considerations have to be integrated in the design of wastewater treatment plants, e.g., higher levels of removal efficiency of contaminants, and energy and nutrient recovery. To facilitate direct water reuse, research programs for wastewater treatment must be directed towards technologies that require less non-renewable energy sources, reduce the use of hazardous chemicals, and remove contaminants.

Several Life Cycle Assessment studies of wastewater treatment systems have been evaluating competing technologies and consistently identifying the strong influence that energy consumption has on the overall environmental impact. Not to mention the strong influence that also sludge handling and disposal process have on the overall environmental impact.

In light of these aspects of wastewater treatment, [Chap. 1](#) presents the advantages linked to the application of chemically assisted primary sedimentation (CAPS); this enables energy optimization of wastewater treatment plants and points to the possibility of wastewater as a possible resource. The increase in production of primary sludge obtained in CAPS generates a major production of biogas in anaerobic digestion which can off-set the power used for the treatment process, thus reducing the use of non-renewable energy. In addition, this chapter discusses the use of organic coagulants such as chitosan (which has a much lower cost) in the CAPS process.

In recent years, there has been increasing concern about the release of contaminants such as endocrine disruptors compounds (EDCs), pharmaceuticals and personal care products (PPCPs) into the environment. These contaminants are ubiquitous, persistent and biologically active, and they may cause disruption of endocrine systems as well as affect the hormonal control of development in aquatic and terrestrial biota. Because the majority of emerging compounds are detectable in the environment at concentrations ranging in ng/L to µg/L levels, [Chap. 2](#) discusses the analytical problems related to the analytical detection of pollutants and of their transformation products.

The effluent from urban wastewater treatment plants (UWWTPs) are among the major sources involved in surface water contamination by EDCs/PPCPs. Hundreds of tons of pharmacological substances enter UWWTPs each year, and very likely they would not be degraded by the physical and biological processes, thus contributing to widespread environmental pollution. The likelihood of water contamination with emerging pollutants as a result of discharge of UWWTP effluents depends on several factors. Among them the most important are: (i) the physico-chemical properties of pollutants; (ii) the wastewater treatment technology in use; (iii) the type of activated sludge process, and (iv) the climatic conditions (such as rainfall, temperature and sunlight). Activated sludge has been the most frequently used biological process in wastewater treatment plants. However, its effectiveness in the removal of emerging contaminants has been recently questioned leading to the employment of advanced processes. A number of investigators have addressed this issue over the past decade highlighting the promising role of a special class of oxidation techniques defined as advanced oxidation processes (AOPs). Other studies have focused on membrane bioreactors (MBR) to treat emerging contaminants from water and wastewater. A brief description of MBR principles and technology is presented in [Chap. 3](#), with updated figures showing the distribution of these plants worldwide. Based on literature data, the efficiency of MBR plants for removing trace pollutants is compared with conventional systems. Finally, there is a discussion on the “green” character of MBR technology.

[Chapter 4](#) evaluates the application of Wet Oxidation (WO) for the treatment of aqueous effluents to remove trace pollutants, based on flow rate and organic content in the wastewater effluent.

[Chapter 5](#) is a review of the application of Photo-Fenton process and complementary treatment systems ($\text{H}_2\text{O}_2/\text{UV-C}$ and Fenton’s reagent) for the

degradation of two industrial pollutant categories with significant endocrine disrupting properties: alkyl phenols (nonyl and octyl phenols) and bisphenol A.

All chapters include fundamentals of the processes investigated as well “green aspects” of technologies that will offer students, technicians, and academics the opportunity to evaluate and select the technologies that lead to better and more sustainable treatment.

Salerno, October 2011

Giusy Lofrano

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Salerno, October 2011

Giusy Lofrano

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Abbreviations

ADBI	4-Acetyl-1,1-dimethyl-6-tert-butylindane
AHMI	6-Acetyl-1,1,2,3,3,5-hexamethylindane
AHTN	7-Acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene
AMBI	5-Amino-6-methyl-2-benzimidazolone
AOPs	Advanced oxidation processes
AOX (RCI)	Adsorbable organically bound halogens
APs	Alkyl phenols
APEOs	Alkyl phenol ethoxylates
ATII	5-Acetyl-1,1,2,6-tetramethyl-3-isopropylindane
BE	Benzoylcgonine
BOD5	Biochemical oxygen demand
BPA	Bisphenol A
BSA	N,O-bis(trimethylsilyl)-acetamide
BSTFA	N,O-bis(trimethylsilyl)-trifluoroacetamide
CAS	Conventional activated sludge
CAPS	Chemically assisted primary sedimentation
CE	Cocaethylene
CEPT	Chemically enhanced primary treatment
CLLE	Continuous liquid–liquid extraction
$C_2O_4^{2-}$	Oxalate ion
$C_2O_4^{\bullet-}$	Oxalate radical
COD	Chemical oxygen demand
DEET	N,N diethyl-m-toluamide
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DNOM	Dissolved natural organic matter
DPMI	6,7-Dihydro-1,1,2,3,3-pentamethyl-4-(5H)-indanone
ECD	Electron capture detector

EDCs	Endocrine disruptors compounds
EDDP	2-Ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine perchlorate
EI	Electron impact
EPA	Environmental protection agency
Fe(IV)	Ferrate
FID	Flame ionization detector
FS	Plat-and-frame/flat sheet
GC	Gas chromatography
GCB	Graphitized carbon black
GLKM	General lumped kinetic model
HHCB	1,2,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-c-2-benzopyrane
HF	Hollow fiber
HO [•]	Hydroxyl radical(s)
HO _{ss} [•]	Steady-state hydroxyl radical concentration
HO ₂ [•]	Hydroperoxyl radical(s)
HPLC	High performance liquid chromatography
iMBR	immersed MBR configuration
IT	Ion trap
KDIE	Kinetic deuterium isotope effect
L	Organic ligand
LITs	Linear ion traps
LC	Liquid chromatography
LLE	Liquid–liquid extraction
LMCT	Ligand to metal charge transfer
LOEC	Lowest observed effect concentration
LSD	Lysergic acid diethylamide
MBR	Membrane bio reactors
MCF	Methyl chloroformate
MDA	3,4-Methylenedioxyamphetamine
MDE or MDEA	Methylenedioxy-ethylamphetamine
MDMA	3,4-Methy-138 lenedioxyamphetamine hydrochloride
MIPs	Molecularly imprinted polymers
MLVSS	Mixed liquor volatile suspended solids
MS/MS	Tandem mass spectrometric
MSTFA	N-Methyl-N trimethylsilyltrifluoroacetamide
MT	(Multi)tubular
MTBSTFA	N-(Tert-butyl dimethylsilyl)-N Methyltrifluoroacetamide

NCI	Negative chemical ionization
NOEC	No observed effect concentration
NP	4-Nonylphenol
NPEOs	Nonylphenol ethoxylates
NPEO-9	Nonylphenol ethoxylate-9
NPEO-10	Ten-fold ethoxylated nonylphenol
NP1EO	4-Nonylphenol monoethoxylate
NP2EO	4-Nonylphenol diethoxylate
O ₂ ^{•-}	Superoxide radical(s)
OECD	Organization for economic cooperation and development
OP	Octylphenol
OPEOs	Octylphenol ethoxylates
PCPs	Personal care products
PPCPs	Pharmaceuticals and personal care products
PFA	Pentafluoropropionic acid anhydride
QqQ	Quadrupole
QqLIT	Quadrupole–linear ion trap
QqTOF	Quadrupole–time of flight
RLU	Relative light units
sMBR	sidestream MBR configuration
SPE	Solid phase extraction
SPME	Solid phase micro extraction
SRT	Solid retention time
TBS	Tert-butyldimethylsilyl
THC	D9-tetrahydrocannabinol
TKN	Total Kjeldahl Nitrogen
TMS	Trimethylsilyl
TMS-DEA	N,N-diethyltrimethylamine
TOC	Total organic carbon
TOD	Total oxygen demand
TrBA	Tri- <i>n</i> -butylamine
TMS-DEA	N,N-diethyltrimethylamine
TSS	Total suspended solids
UV	Ultra violet
UWWTP	Urban wastewater treatment plants
VSS	Volatile suspended solids
WAO	Wet air oxidation
WO	Wet oxidation

WPO	Wet peroxidation
WWTPS	Wastewater treatment plants
YES	Yeast estrogen screen
4-CP	Chlorophenol
4-OP	4-tert-octylphenol
4-NP	4-nonylphenol