Environmental Chemistry for a Sustainable World 66

Nadia Morin-Crini
Eric Lichtfouse
Grégorio Crini *Editors*

Emerging Contaminants Vol. 2

Remediation

Springer

Environmental Chemistry for a Sustainable World

Volume 66

Other Publications by the Editors

Books
Environmental Chemistry
http://www.springer.com/978-3-540-22860-8

Organic Contaminants in Riverine and Groundwater Systems
http://www.springer.com/978-3-540-31169-0

Sustainable Agriculture
Volume 1: http://www.springer.com/978-90-481-2665-1
Volume 2: http://www.springer.com/978-94-007-0393-3

Book series
Environmental Chemistry for a Sustainable World
http://www.springer.com/series/11480

Sustainable Agriculture Reviews
http://www.springer.com/series/8380

Journal
Environmental Chemistry Letters
http://www.springer.com/10311

More information about this series at http://www.springer.com/series/11480

Nadia Morin-Crini • Eric Lichtfouse
Grégorio Crini
Editors

Emerging Contaminants Vol. 2

Remediation

Springer

Editors
Nadia Morin-Crini
Chrono-environnement, UMR 6249
Université Bourgogne Franche-Comté
Besançon, France

Grégorio Crini
Chrono-Environnement, UMR 6249
Université Bourgogne Franche-Comté
Besançon, France

Eric Lichtfouse
Aix Marseille University, CNRS, IRD,
INRA, Coll France, CEREGE
Aix en Provence, France

ISSN 2213-7114 ISSN 2213-7122 (electronic)
Environmental Chemistry for a Sustainable World
ISBN 978-3-030-69089-2 ISBN 978-3-030-69090-8 (eBook)
https://doi.org/10.1007/978-3-030-69090-8

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

Man's use of pollutants began to affect the environment during the Industrial Revolution. Today, we are in the Pollutant Removal Age.

Grégorio Crini, 2010

Figure. An aerated lagoon to treat wastewaters from a pulp and paper industry; source: G. Crini

This book, entitled *Remediation of Emerging Contaminants*, is the second volume on emerging contaminants published in the series Environmental Chemistry for a Sustainable World and written by 64 international contributors from 24 countries. The first volume provides an overview of on emerging contaminants, their presence in the water compartment, and their potential health effects. This second volume focuses on methods for remediation of emerging contaminants.

The first chapter by Nadia Morin-Crini et al. details chemical and biological methods for the removal of emerging contaminants in water. The second chapter by Borislav Malinović et al. reviews the electrochemical treatments for removing pollutants. In Chap. 3, Eric Lichtfouse et al. present technologies for removing selenium from water and wastewater. The final chapter by Grégorio Crini et al. summarizes advanced treatments for the removal of alkylphenols and alkylphenol polyethoxylates from wastewater.

The editors extend their thanks to all the authors who contributed to this book for their efforts in producing timely and high-quality chapters. The creation of this book would not have been possible without the assistance of several colleagues and friends deserving acknowledgment. They have helped by choosing contributors and reviewing chapters and in many other ways. Finally, we would like to thank the staff at Springer Nature for their highly professional editing of the publication.

Besançon, France Nadia-Morin Crini

Aix en Provence, France Eric Lichtfouse

Besançon, France Grégorio Crini

Contents

Contributors

Idil Arslan Alaton Istanbul Technical University, Istanbul, Turkey

Mehran Aliaskari Institute for Advanced Membrane Technologies (IAMT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Eggenstein-Leopoldshafen, Germany

Mondher Barhoumi Faculté des Sciences Bizerte, Zarzouna, Tunisia

Youssef-Amine Boussouga Institute for Advanced Membrane Technologies (IAMT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Eggenstein-Leopoldshafen, Germany

Corina Bradu Department of Systems Ecology and Sustainability, PROTMED Research Centre, University of Bucharest, Bucharest, Romania

Irena Kralj Cigić Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia

Cesare Cosentino Istituto di Chimica e Biochimica G. Ronzoni, Milan, Italy

Grégorio Crini Laboratoire Chrono-environnement, UMR 6249, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, Besançon, France

Soumya Das Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK, Canada

Sébastien Déon Institut UTINAM, UMR CNRS 6213, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, Besançon, France

Ján Derco Institute of Chemical and Environmental Engineering, Department of Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava 1, Slovak Republic

Éva Fenyvesi CycloLab Cyclodextrin Research and Development Ltd, Budapest, Hungary

Patrick Fievet Institut UTINAM, UMR CNRS 6213, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, Besançon, France

Marc Fourmentin Université du Littoral Côte d'Opale, Laboratoire de Physico-Chimie de l'Atmosphère (LPCA, EA 4493), ULCO, Dunkerque, France

Liliana Giraldo Facultad de Ciencias, Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia

Andreja Žgajnar Gotvajn Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia

Mohammad Mahmudul Huq Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Canada

Michihiko Ike Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan

Daisuke Inoue Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, Japan

Masashi Kuroda Graduate School of Environmental and Disaster Research, Tokoha University, Shizuoka, Shizuoka, Japan

Eric Lichtfouse Aix Marseille University, CNRS, IRD, INRA, Coll France, CEREGE, Aix en Provence, France

Monica Magureanu Department for Plasma Physics and Nuclear Fusion, National Institute for Lasers, Plasma and Radiation Physics, Magurele, Romania

Borislav N. Malinović Faculty of Technology, University of Banja Luka, Banja Luka, Bosnia and Herzegovina

Francesca Mapelli Biotechnology and Environmental Microbiology Lab-BEaM Lab, Department of Food, Environmental and Nutritional Sciences (DeFENS), University of Milan, Milan, Italy

Jernej Markelj Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia

Juan Carlos Moreno-Piraján Facultad de Ciencias, Departamento de Química, Grupo de Investigación en Sólidos Porosos y Calorimetría, Universidad de los Andes (Colombia), Bogotá, Colombia

Nadia Morin-Crini Laboratoire Chrono-Environnement, UMR 6249, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, Besançon, France

Constantinos Noutsopoulos Sanitary Engineering Laboratory, Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Athens, Greece

Lorenzo A. Picos-Corrales Facultad de Ciencias Químico Biológicas, Universidad Autónoma de Sinaloa, Ciudad Universitaria, Culiacán, Sinaloa, Mexico

Helena Prosen Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia

Ana Rita Lado Ribeiro Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Porto, Portugal

Olim Ruzimuradov Turin Polytechnic University in Tashkent, Tashkent, Uzbekistan

Andrea Iris Schäfer Institute for Advanced Membrane Technologies (IAMT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Eggenstein-Leopoldshafen, Germany

Tamás Sohajda CycloLab Cyclodextrin Research and Development Ltd, Budapest, Hungary

Jafar Soltan Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Canada

Maria Concetta Tomei Istituo di Ricerca sulle Acque, Consiglio Nazionale delle Ricerche, Monterotondo, Italy

Giangiacomo Torri Istituto di Chimica e Biochimica G. Ronzoni, Milan, Italy

Melissa Gurgel Adeodato Vieira Department of Processes and Products Design, School of Chemical Engineering, University of Campinas, Campinas, SP, Brazil

Martin Vrabel' Institute of Chemical and Environmental Engineering, Department of Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava 1, Slovak Republic

Lee D. Wilson Department of Chemistry, University of Saskatchewan, Saskatoon, SK, Canada

About the Editors

Nadia Morin-Crini is an analytical chemist at the University of Bourgogne Franche-Comté, Besançon, France. Her research interests include the extraction and analysis of chemicals from various solid and liquid environmental matrices. She is responsible for a technological platform that studies old and present environments. She has published more than 130 papers in peer-reviewed scientific journals.

Eric Lichtfouse is a geochemist and professor of scientific writing at Aix-Marseille University, France. He has invented carbon-13 dating and published the book *Scientific Writing for Impact Factor Journals*. He is chief editor of the journal *Environmental Chemistry Letters* and the book series Sustainable Agriculture Reviews and Environmental Chemistry for a Sustainable World.

Grégorio Crini is an environmental polymer scientist at the University of Bourgogne Franche-Comté, Besançon, France. His research activities focus on the design of new polymer networks and the environmental aspects of polysaccharide chemistry. He has published more than 210 papers in international journals and is a highly cited researcher with an h-index of 40 and more than 13,000 citations.

Abbreviations

ACF	Activated carbon fiber
AOP	Advanced oxidation process
AOPs	Advanced oxidation processes
BDD	Boron-doped diamond electrode
BGA	Boron-doped graphene aerogel
BOD	Biological oxygen demand
BPA	Bisphenol A
CB	Conductive band
CCM	Coal-based carbon membrane
CE	Counter electrode
CF	Carbon fiber
COD	Chemical oxygen demand
D_{ow}	pH-dependent *n*-octanol-water distribution ratio
DC	Divided cell
E1	Estrone
E2	17-beta-estradiol
EC	European Commission
EE2	17-alpha-ethinylestradiol
FD	Frequency of detection
GC	Glassy carbon
GC-MS	Gas chromatography coupled with mass spectrometry
GM	Galvanostatic mode
GUS	Groundwater ubiquity score
HPLC	High-performance liquid chromatography
HPLC-UV	High-performance liquid chromatography with UV detection
HQ	Hazard quotient
HR	Hazard ratio
IQR	Interquartile range
ISPRA	Italian National Institute for Environmental Protection and Research
K_{oc}	Partition coefficient between soil organic carbon and water
K_{ow}	n-octanol-water partition coefficient

LC-MS/MS	Liquid chromatography coupled with (tandem) mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
LS	Light source
MEC	Measured environmental concentrations
n.d.	Not detected
OR	Odds ratio
pK_a	The negative base-10 logarithm of the acid dissociation constant (K_a) of a solution
PM	Potentiostatic mode
PM	Particulate matter
PM_{10}	Coarse particulate matter
$PM_{2.5}$	Fine particulate matter
$PM_{0.1}$	Ultrafine particulate matter
PNEC	Predicted no-effect concentration
SCE	Saturated calomel electrode
S_w	Water solubility
SHE	Standard hydrogen electrode
SS	Stainless steel
TOC	Total organic carbon
UC	Undivided cell
VB	Valence band
WE	Working electrode
WWTP	Wastewater treatment plant
ZVI	Zero-valent ion

Chapter 1
Remediation of Emerging Contaminants

Nadia Morin-Crini, Eric Lichtfouse, Marc Fourmentin, Ana Rita Lado Ribeiro, Constantinos Noutsopoulos, Francesca Mapelli, Éva Fenyvesi, Melissa Gurgel Adeodato Vieira, Lorenzo A. Picos-Corrales, Juan Carlos Moreno-Piraján, Liliana Giraldo, Tamás Sohajda, Mohammad Mahmudul Huq, Jafar Soltan, Giangiacomo Torri, Monica Magureanu, Corina Bradu, and Grégorio Crini

Abstract Water pollution by emerging contaminants has become a major source of concern and a priority for society and public authorities. Emerging contaminants are a group of natural and synthetic chemicals and biological agents that are not routinely monitored or regulated in the environment and may have known or suspected

N. Morin-Crini (✉)
Laboratoire Chrono-environnement, UMR 6249, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, Besançon, France
e-mail: nadia.crini@univ-fcomte.fr

E. Lichtfouse
Aix Marseille University, CNRS, IRD, INRA, Coll France, CEREGE, Aix-en-Provence, France
e-mail: eric.lichtfouse@inrae.fr

M. Fourmentin
Université du Littoral Côte d'Opale, Laboratoire de Physico-Chimie de l'Atmosphère (LPCA, EA 4493), Dunkerque, France
e-mail: marc.fourmentin@univ-littoral.fr

A. R. L. Ribeiro
Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Porto, Portugal
e-mail: ritalado@fe.up.pt

C. Noutsopoulos
Sanitary Engineering Laboratory, Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, Athens, Greece
e-mail: cnoutso@central.ntua.gr

F. Mapelli
Biotechnology and Environmental Microbiology Lab-BEaM Lab, Department of Food, Environmental and Nutritional Sciences (DeFENS), University of Milan, Milan, Italy
e-mail: francesca.mapelli@unimi.it

N. Morin-Crini et al. (eds.), *Emerging Contaminants Vol. 2*, Environmental Chemistry for a Sustainable World 66,
https://doi.org/10.1007/978-3-030-69090-8_1

adverse effects on the environment and human health. The list of these substances is particularly long and includes pharmaceuticals, personal care products and cosmetics, pesticides, surfactants, industrial products and additives, nanoparticles and nanomaterials, and pathogens. Many emerging contaminants are released continuously into the environment and can cause chronic toxicity even at low concentra-

É. Fenyvesi
CycloLab Cyclodextrin Research and Development Ltd, Budapest, Hungary
e-mail: fenyvesi.e@cyclolab.hu

M. G. A. Vieira
Department of Processes and Products Design, School of Chemical Engineering, University of Campinas, Campinas, SP, Brazil
e-mail: melissagav@feq.unicamp.br

L. A. Picos-Corrales
Facultad de Ciencias Químico Biológicas, Universidad Autónoma de Sinaloa, Ciudad Universitaria, Culiacán, Sinaloa, Mexico
e-mail: lorenzo.picos.c@uas.edu.mx

J. C. Moreno-Piraján
Facultad de Ciencias, Departamento de Química, Grupo de Investigación en Sólidos Porosos y Calorimetría, Universidad de los Andes (Colombia), Bogotá, Colombia
e-mail: jumoreno@uniandes.edu.co

L. Giraldo
Facultad de Ciencias, Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia
e-mail: lgiraldogu@unal.edu.co

T. Sohajda
CycloLab Cyclodextrin Research and Development Ltd, Budapest, Hungary
e-mail: sohajda@cyclolab.hu

M. M. Huq · J. Soltan
Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Canada
e-mail: shafi.huq@usask.ca; j.soltan@usask.ca

G. Torri
Istituto di Chimica e Biochimica G. Ronzoni, Milano, Italy
e-mail: torri@ronzoni.it

M. Magureanu
Department for Plasma Physics and Nuclear Fusion, National Institute for Lasers, Plasma and Radiation Physics, Magurele, Romania
e-mail: monica.magureanu@inflpr.ro

C. Bradu
Department of Systems Ecology and Sustainability, PROTMED Research Centre, University of Bucharest, Bucharest, Romania
e-mail: corina.bradu@g.unibuc.ro

G. Crini
Laboratoire Chrono-environnement, UMR 6249, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, Besançon, France
e-mail: gregorio.crini@univ-fcomte.fr

tions, endocrine disruption in humans and aquatic life, and the development of antibiotic resistant bacteria. It is therefore necessary to mobilize efforts to protect human health and biodiversity.

Two of the main sources of emerging contaminants are wastewater treatment discharges and agricultural practices. However, conventional wastewater treatment plants have not been designed to remove such contaminants. It is therefore important to develop effective treatment methods capable of eliminating the parent emerging molecules and their metabolites. This is a difficult and challenging task because most of emerging contaminants are recalcitrant substances. The methods must also target not only water chemicals but also water microbiols in order to reduce and eliminate the toxicity and impact of the treated wastewater.

During the past two decades, several physical, chemical and biological technologies have been proposed for emerging contaminant removal. Each technology has its own advantages and constraints not only in terms of cost, but also in terms of efficiency, feasibility, and environmental impact. However, among the various treatment processes currently cited for wastewater treatment, only few are commonly employed by the industrial sector for technological and economic reasons. Extensive research on this topic highlights the growing interest of scientists in developing treatment systems that are increasingly effective in removing mixtures of trace pollutants, simple to implement from a technological point of view, economically viable and environmentally friendly, with little or no impact on the environment.

The objective of this chapter is to present the recent state of knowledge on the advanced treatments proposed for the removal of emerging contaminants in wastewater when they are present in trace amounts in wastewater. After general considerations on wastewater treatment plant, the first part is focused on adsorption-oriented processes using conventional (activated carbon, clays) or non-conventional (cyclodextrin polymers, metal-organic frameworks, molecularly imprinted polymers, chitosan, nanocellulose) adsorbents. Biosorbents such as cyclodextrin bead polymers have great potential in environmental applications although they are still at the laboratory study stage. The second part presents examples of biological-based technologies for the degradation and elimination of emerging contaminants. Selected biological approaches include constructed wetlands, biomembrane reactors, strategies based on the use of algae, fungi and bacteria, and enzymatic degradation. The third part briefly presents the membrane filtration strategy that is already used as a tertiary treatment. The final part is focused on advanced oxidation processes that also represent one of the most promising strategies because of their simplicity and efficiency.

Keywords Emerging contaminants · Substances of global concern · Pharmaceuticals · Personal care products · Pesticides · Water pollution · Aquatic compartments · Wastewater treatment plants · Remediation · Bioremediation · Conventional removal technologies · Advanced treatments · Adsorption · Biosorption · Cyclodextrin polymers · Constructed wetlands · Membrane bioreactor technology · Membrane filtration · Disinfection · Ozonation · Advanced oxidation processes · Catalytic ozonation · Non-thermal plasma

1.1 Introduction

Emerging contaminants such as pharmaceuticals and personal care products represent a new global water quality challenge, with potentially serious threats to human health and the environment, including water resources. Indeed, the presence of emerging contaminants and biological agents in treated and untreated water has received increasing attention because the risk they pose to human health, ecosystems and water resources is not yet fully understood. For example, antibiotics and endocrine disruptors are among the best examples of "new" contaminants that are known to the public and are of concern. Traces of these substances are being found in water resources, including drinking water, throughout the world. Numerous studies on the presence and behavior of pharmaceuticals in the environment have demonstrated negative effects to aquatic ecosystems and wildlife in general. Another worrying phenomenon is the emergence of antibiotic resistance. Overuse of antibiotics has encouraged the development of antibiotic-resistant strains. Antibiotic resistant bacteria and antibiotic resistance genes pose a public health concern when they transfer antibiotic resistance to human pathogens. All these topics are of great interest to the scientific community and concern to our societies.

The term emerging contaminants includes chemical or biological contaminants without a clearly defined regulatory status. They are often substances, not necessarily of new use, but newly identified, for which data concerning their presence, their fate in the environment and their potential impacts on health or the environment are patchy. Among the emerging pollutants are, in particular, pharmaceuticals subject or not to medical prescription (antibiotics, hormones, illicit drugs, etc.) for human or veterinary use, products for daily use (personal care products, cosmetics, detergents, disinfectants, antioxidants, etc.), products of industrial origin (surfactants, additives, solvents, flame retardants, nanoparticles, etc.), pesticides, and pathogens. The number of molecules concerned is constantly changing both in terms of parent substances and their degradation products (metabolites, for example resulting from biological treatment). In general, these synthetic or naturally occurring chemicals are not commonly monitored in the environment and they are consistently being found not only in wastewaters but also in water resources (groundwater, surface water), and even in drinking water.

Conventional domestic wastewater treatment plants (often stabilization ponds, activated sludge systems) were not designed to treat recalcitrant organic pollutants including emerging substances (Bolong et al. 2009; Teijón et al. 2010; Jelic et al. 2011; Verlicchi et al. 2012; Petrie et al. 2015; Machado et al. 2016; Priac et al. 2017; Botero-Coy et al. 2018; Gogoi et al. 2018; Tolboom et al. 2019; Patel et al. 2019). It is also important to point out that the elimination of microorganisms is not an objective of wastewater treatment plants either (Morin-Crini and Crini 2017). Botero-Coy et al. (2018) reported that the concentrations of some pharmaceuticals (e.g. erythromycin, metronidazole, sulfamethoxazole) in the effluent from a municipal wastewater treatment plant (Bogotá, Colombia) were even higher than in influent, suggesting negative removal efficiencies. Jelic et al. (2011) and Verlicchi et al. (2012) previously reported similar results within European effluents, suggesting that the wastewater treatment plants act as a concentrator of contaminants. This incomplete removal evidences the need of alternative or complementary treatment technologies (Jelic et al. 2011; Verlicchi et al. 2012; Botero-Coy et al. 2018; Serna-Galvis et al. 2019). Conventional water treatments often involve a combination of methods such as sand filtration coupled with a coagulation pre-treatment, + adsorption + disinfection step, which are usually not effective to remove emerging pollutants. It is therefore important to develop effective treatment methods capable of eliminating not only the parent emerging molecules but also their metabolite and transformation products. These methods must also meet not only water chemistry objectives (particularly in terms of chemical abatement of the residual pollutant load and quality standards) but also water microbiology objectives, in order to reduce and eliminate the toxicity and environmental impact of the treated wastewater. These are two research topics that have been mobilizing the scientific community.

After general considerations on wastewater treatment plants, this chapter presents and discusses advanced treatment methods such as adsorption-oriented processes, biological-based technologies, membrane filtration and advanced oxidation processes. In each of the sections, a state of the art was first conducted and then the authors' research is presented to illustrate each water treatment technology.

1.2 Municipal Wastewater Treatment Plants

Human use of chemicals such as metals began to affect the environment during the "Industrial Revolution" of the second half of the eighteenth century. Since the end of the Second World War, the use of chemical, pharmaceuticals and agrochemical products has greatly increased over the years to meet the growing needs of consumers, who are also rising in number. However, economic development has been accompanied by environmental problems including water pollution. In response to this pollution problem, the first wastewater treatment plants were set up in the 1960s in France, for example. The first European regulations on aqueous discharges appeared a decade later. Today, we are in the "Emerging Pollutant Removal Age" (Crini and Lichtfouse 2018a, b) and, it is, therefore, not surprising that there have been considerable efforts to develop technologies to reduce contaminant emissions. Indeed, the presence of pesticides, pharmaceuticals and personal care products in water challenges the scientific community and water treatment stakeholders to find simple, practical, inexpensive, effective and environmentally friendly disposal solutions.

An important question arises: how do rivers receive emerging contaminants? It is now recognized that the presence in aquatic environments is mainly correlated with the discharge of effluents from municipal wastewater treatment plants (Fig. 1.1), with a higher incidence in wastewater treatment plants in highly industrialized and urban areas (Sole et al. 2000; Goméz et al. 2006; Stackelberg et al. 2007; Kasprzyk-Hordern et al. 2008; Watkinson et al. 2009; Basile et al. 2011; Gonzalez et al. 2012; Meffe and Bustamante 2014; Machado et al. 2016; Morin-Crini and Crini 2017;

Fig. 1.1 Over-consumption of pharmaceuticals and personal care products and contamination of rivers by the same substances present in wastewater from sewage treatment plants. (Region: Sinaloa, Mexico; source: Lorenzo A. Picos-Corrales, Sinaloa, Mexico)

Priac et al. 2017; Gilabert-Alarcón et al. 2018; Mezzelani et al. 2018; Picos-Corrales et al. 2020). However, environmental contamination/pollution originates not only from domestic activity but also from the industrial and agricultural sectors, and other activities such as transport (Morin-Crini and Crini 2017). Indeed, even if all discharges comply with regulations, industrial and urban wastes can still contain a mixture of substances, known or unknown (metabolites, degradation products), and their concentration varies from a few ng/L to a few mg/L. All the substances we use in our daily lives, such as pharmaceuticals or personal care products, can enter the environment through excretion in human and animal urine and feces, through the flushing of unused medicines, or through our domestic uses (cooking, bathing), and results in nanogram per liter to microgram per liter, even after adequate treatment.

For example, Watkinson et al. (2009) investigated the presence of 28 antibiotics in several Australian water matrices, including six rivers and drinking water. The results showed that four substances, i.e., monensin, erythromycin, sulfamethoxazole and norfloxacin, were more frequently detected in surface water, at concentrations ranging from low ng/L to 2.0 μg/L. The authors demonstrated that in one river that did not receive discharges from municipal wastewater treatment plants, the total concentration of the investigated antibiotics was significantly lower than those in the other five rivers, suggesting that municipal wastewater treatment plants were an important source of antibiotics to the streams. Meffe and Bustamante (2014), Machado et al. (2016) and Gilabert-Alarcón et al. (2018) reported similar conclusions in Italian, Brazilian and Mexican water resources, respectively.

When wastewater is contaminated and remediation becomes necessary, the best purification approach should be chosen to reach the decontamination objectives as established by legislation (Crini and Badot 2007, 2010; Morin-Crini and Crini 2017). A purification process generally consists of five successive steps: (1) preliminary treatment or pre-treatment (physical & mechanical); (2) primary treatment (physicochemical & chemical); (3) secondary treatment or purification (chemical & biological); (4) tertiary or final treatment (physical & chemical); and (5) treatment of the sludge formed (gravity or mechanical thickening and dewatering, drying or incineration). In general, the first two steps are gathered under the notion of pre-treatment or preliminary step, depending on the situation. Pre-treatment removes debris and large solids, while primary treatment focuses on the removal of an appreciable load of organic matter and suspended solids from the influent. This pre-treatment stages, which can be carried out using mechanical or physical means, is indispensable before envisaging secondary treatment because particulate pollution (e.g. suspended solids, colloids, fats, etc.) hinders the posterior treatment, making it less efficient or damaging the decontamination equipment. Primary chemical treatment such as pH adjustment or pre-reduction of a high organic load may also be required. Before its discharge into the environment or its reuse, the pre-treated effluent must undergo secondary purification treatment using in most cases biological processes to produce a satisfactory final effluent. In certain cases, a final or tertiary treatment (including disinfection) can also be required to remove the remaining pollutants or the molecules produced during the secondary purification.

Around the world, almost the same wastewater treatment scheme is used by following the same steps above listed. From a water engineering point of view, the only difference is the type of matrix to be treated (domestic, industrial or drinking). In general, for municipal/domestic wastewaters treatment, the removal of pollutants from the raw wastewater is primarily achieved by biological means (often activated sludge systems). Indeed, biodegradation is one of the main treatment applied to decontaminate wastewater. For industrial wastewaters, e.g. from textile, pulp and paper or surface-treatment industry, pollutant removal is achieved by physical (sand filtration, adsorption onto carbons, membrane filtration, evaporation, extraction), chemical (precipitation, oxidation, electrocoagulation, electrochemical treatment, ion-exchange using organic resins) and biological (lagoon, membrane bioreactors) means, with research focusing on more efficient and less expensive systems combinations or new alternatives such as biosorption, biomass, advanced oxidation processes. In general, precipitation is – together with adsorption – one of the two main treatments applied at industrial scale (Crini and Badot 2007, 2010; Crini 2010). For the production of drinking water, filtration (sand, carbon) and adsorption (activated carbon) steps are used, coupled with coagulation/flocculation and disinfection (ozonation or chlorination) steps.

The main objective of a conventional municipal wastewater treatment plant, receiving raw wastewater from domestic and industrial discharges, is to remove organic matter and nutrients, e.g. nitrogen and phosphorus. A technological process widely used in the world is the so-called activated sludge, due to its competitive cost and high efficiency. Currently, under optimized conditions, more than 95% of organic and mineral substances can be eliminated by biological-based methods used in municipal wastewater treatment plants. In general, these performance levels make possible to meet the regulatory requirements for the list of substances and water parameters analyzed. However, the efficiency of a conventional system varies depending on the wastewater characteristics and the treatment process used, e.g. activated sludge, membrane biological reactor, with a possible combination with a chemical treatment.

As already mentioned, existing conventional wastewater treatment plants and drinking water treatment plants were not designed to remove pharmaceuticals or nanoparticles, which are difficult to biodegrade or filter, respectively. For example, substances such as acetylsalicylic acid, diclofenac, carbamazepine, atenolol or propranolol are difficult to degrade by conventional biological treatment: performance is estimated to be less than 10% (Patel et al. 2019). Several studies have nevertheless showed that certain substances such as endocrine disruptor compounds can be reduced (Priac et al. 2017; Gogoi et al. 2018; Patel et al. 2019).

In a wastewater treatment plant, besides biodegradation, adsorption to sludge is the most effective process to eliminate substances. Numerous substances are poorly soluble hydrophobic compounds, poorly biodegradable and present a strong affinity for sludge. A typical example is the anti-inflammatory diclofenac that can be partially adsorbed on sludge (Barbosa et al. 2016). In Europe, treated sludge after stabilization is often disposed in the soil or reused for agricultural purposes and composting. A previous study by Johnson and Sumpter (2001) revealed that the essential sewage treatment can rapidly convert organics into biomass that is then separated from the effluent phase by settlement. However, not all compounds were completely broken down or converted into biomass in that study. For example, the steroid estrogens found in effluent corresponded to the products of incomplete breakdown of their respective parent molecules. Liu et al. (2009) also reported that endocrine disruptor compounds were not completely removed by municipal wastewater treatment plants and remained at fluctuating concentrations in the effluent. Thus, the discharge of such water may be the main reason for the wide distribution and occurrence of emerging contaminants in surface waters.

The lists of substances monitored by the treatment plants are beginning to evolve, which will eventually force the plants to upgrade their operations to better treat wastewater. There are two main policies for water pollution control: the first is to focus on reducing pollutant emissions at source, e.g. France, and the second is to focus on downstream reduction at treatment plants, e.g. in Switzerland and Germany (Morin-Crini and Crini 2017). In the latter case, tertiary treatment is required. This final treatment is necessary to remove the remaining pollutants such as pharmaceuticals and their metabolites. However, the use of tertiary treatment worldwide, including in Europe, is still limited due to significant economic costs. However, it may be necessary in the future if further restrictions are applied (Crini and Lichtfouse 2018a, b).

1.3 Methods for the Removal of Emerging Contaminants

Removing emerging contaminants from wastewater is a difficult and challenging task because most emerging contaminants are recalcitrant substances, often present at trace amounts in complex mixtures. Indeed, a major factor complicating the cleanup of many sites is the coexistence of organic molecules and mineral substances such as metals and metalloids, the so-called mixed wastes. Another complicating factor is the wide range of properties of contaminants, with different chemical structures and functionalities. This diversity of water pollutants requires a wide range of treatment methods that must not only be effective, but also technologically and economically feasible.

To treat emerging contaminants, a multitude of techniques classified as physicochemical treatments, biological treatments, membrane filtration, advanced oxidation technologies, adsorption/biosorption have been proposed in the literature (Fig. 1.2) (Crini and Badot 2007, 2010; Acero et al. 2013; Charles et al. 2014; Secondes et al. 2014; Serna-Galvis et al. 2016, 2019; Bedoya-Ríos and Lara-Borrero 2018; Botero-Coy et al. 2018; Crini and Lichtfouse 2018a, b; Kim et al. 2018).

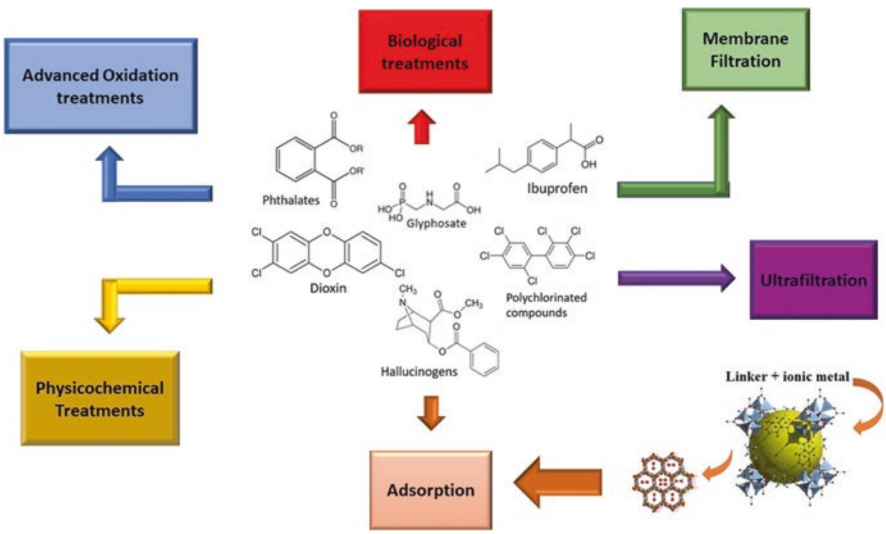

Fig. 1.2 Methods used to remove emerging compounds. (Source: Juan Carlos Moreno-Piraján, Bogotá, Colombia)

Advanced treatments such as biosorption onto non-conventional materials (Wang and Wang 2016; Li et al. 2019a; Fenyvesi et al. 2020; Rojas and Horcajada 2020), filtration membrane coupled with a biological step, algal-based technologies, and oxidation processes combined with an adsorption pretreatment (Serna-Galvis et al. 2016, 2019; Rodriguez-Narvaez et al. 2017) have been proposed to treat domestic water. Recent studies showed that the latter techniques could be a promising way, especially advanced oxidation processes such as ozonation, electrochemistry, photocatalysis, solar-driven processes or solar photo-assisted H_2O_2 treatment (Polo-López et al. 2014; Secondes et al. 2014; Serna-Galvis et al. 2016, 2019). Indeed, advanced oxidation processes have been demonstrated to be very efficient in decreasing not only organic substances but also the pathogen load in contaminated water (Moreira et al. 2016). This is of special interest because of properly treated wastewater could be an alternative renewable water resource, for example for agriculture as an end-use point. All these techniques can also be considered for treating industrial water (Wang and Wang 2016; Crini et al. 2019).

1.4 Adsorption-Oriented Processes for the Removal of Emerging Contaminants

1.4.1 Adsorption of Emerging Contaminants on Activated Carbons

Liquid-solid adsorption/sorption is a key method for removing contaminants, particularly organics, from wastewaters (industrial effluents) or drinking water sources. Indeed, this technique of contaminant removal can produce high quality water, while also being a process that is both technologically simple and economically feasible (Liu and Liptak 2000; Yang 2003; Crini 2010).

Liquid-solid adsorption/sorption involves the accumulation of adsorbate substances from an effluent onto the external and internal surfaces of a material/adsorbent used as a mass separating agent (Crini and Badot 2007, 2010; Fomina and Gadd 2014; Crini and Lichtfouse 2018a, b; Crini et al. 2019; de Andrade et al. 2018; Jeirani et al. 2017). This surface phenomenon is a result of complicated interactions among the three components involved, i.e. the adsorbent, the adsorbate and the effluent (water or wastewater). The data from the literature and also from the industry show that the control of adsorption performances of a solid material in liquid-phase adsorption depends on the following factors: (i) the origin and nature of the solid such as its physical structure, chemical nature and functional groups; (ii) the activation conditions of the raw solid (physical treatment, chemical modifications); (iii) the influence of process variables such as contact time, initial pollutant concentration, solid dosage and dynamic conditions; (iv) the chemistry of the contaminant (as example for an organic molecule, its pKa, polarity, size and functional groups); and finally, (v) the effluent conditions, referring to its pH, ionic strength, temperature and the presence of multi-contaminants and impurities.

Carbon-based materials are one of the oldest and most widely used adsorbents/sorbents, employed since the beginning of the 1900s in the treatment of drinking water (Liu and Liptak 2000; Dąbrowski et al. 2005; Crini and Badot 2007, 2010; Khalaf 2016). These adsorbents have excellent textural properties (high porosity, high specific surface area, large range of particle sizes) and physicochemical properties (surface chemistry) which together account for their excellent adsorption capacity. The process that uses carbons at industrial scale is often carried out by feeding the effluent continuously through a packed bed of carbon (Fig. 1.3). These fixed-bed systems have an important advantage because adsorption depends on the concentration of the substance(s) in the solution being treated. The adsorbent is continuously in contact with fresh effluent; hence, the concentration in the water in contact with a given layer of adsorbent in a column is relatively constant. The process is efficient and economical from the point of view of implementation and operation, which is relatively simple (Geankoplis 1993) and does not generate water by-products as in the case of chemical oxidation or advanced oxidation processes (Rossner et al. 2009; Ahmed et al. 2015; de Andrade et al. 2020), which activities and toxicities still require further studies (Zhang et al. 2016a).

Activated carbons are used as very good adsorbents of a wide range of contaminants and contamination, e.g. to adsorb organic matter in order to reduce the organic load in secondary and tertiary treatment in a municipal wastewater treatment plant, to treat organics such as pesticides, aromatic and phenolic derivatives, volatile aromatics, hydrocarbons and surfactants, to decrease chemical oxygen demand and biological oxygen demand, to discolor water (dye removal) or to treat substances

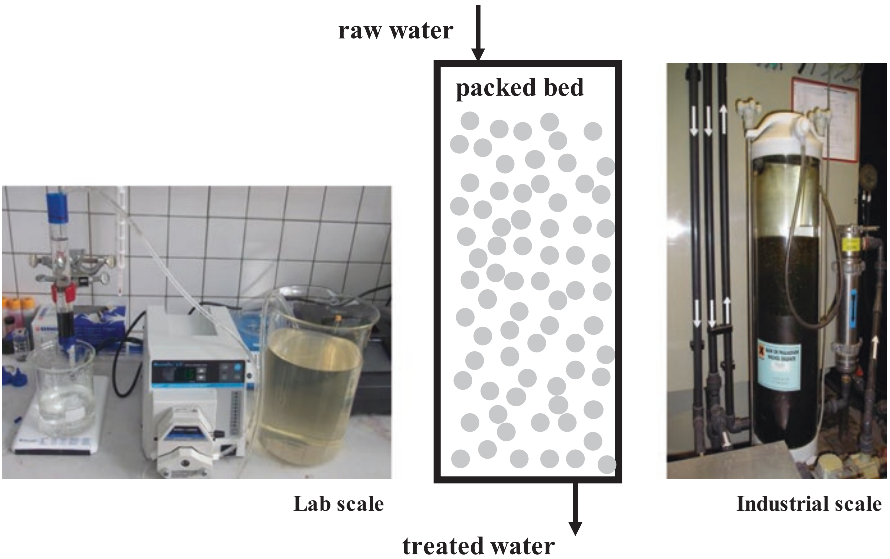

Fig. 1.3 Fixed-bed type process used for adsorption of contaminants from water or wastewater, e.g. for the post-treatment of a pharmaceutical effluent treated by chemical oxidation. (Source: Grégorio Crini, Besançon, France)

that cause specific taste or smell (Crini and Badot 2007, 2010; Couto et al. 2015; Ferreira et al. 2015; Crini et al. 2019; Khan et al. 2020). The adsorption efficiency depends on the type of carbon used, the properties of the adsorbate, as well as the composition of the effluent being treated (Crini and Badot 2010; Ahmed et al. 2015).

Over the past three decades, activated carbons, in granular (GAC) or powder (PAC) form, have been widely used in conjunction with microorganisms for treating wastewater. Macroporous activated carbons can be used as supports for bacteria: the bacteria then degrade part of the adsorbed organic matter (biological elimination) and thus participate in the *in situ* regeneration of the adsorbent. Two combined processes are principally used. Powder activated carbon treatment is obtained by adding carbon to activated sludge. Biological activated carbon (BAC) is a filter made of biofilm-covered granular activated carbon. Commercial activated carbon materials have been employed to remove organic pollutants such as pesticides from wastewater and water. In the purification of drinking water, granular activated carbon filters have commonly been used as a polishing step to remove potentially harmful trace organics. This type of treatment is, in general, coupled to an ozonation stage, further improving the performance of the process. Carbon biological filters are, for instance, used for the detoxification of organic effluent loaded with inorganic ions (removal of iron, manganese, and nitrate). To obtain cost-effective technology (especially in the field of water recycling), carbon powder is used in conjunction with an ultrafiltration membrane or with other techniques, such as oxidation. In Europe, active carbon competes favorably with nanofiltration and begins to replace oxidation with ozone, in particular to remove pesticides (Crini and Badot 2010).

The major advantage of carbon adsorption is that the solid adsorbent can be easily separated from the treated liquid. This allows easy and flexible process operation. However, as it is non-selective, common innocuous organics may interfere with the removal of hazardous compounds. Active carbon technology presents other disadvantages. Active carbons are quite expensive (the higher the quality, the greater the cost). Different qualities of carbon are strongly related to the raw material used, as well as it depends on the carbonization conditions and the way in which activation is performed (physical or chemical). And yet, even though the high absorbing power of active carbons is widely recognized, there are some drawbacks, namely the need of disposal of spent carbons, their rapid saturation, and their regeneration. This regeneration step of saturated carbon is also expensive, not straightforward, and results in loss of the sorbent. Finally, the carbon-adsorption process can be limited in cases of ultra-low concentrations of contaminants (Putra et al. 2009; Lian et al. 2014; Ahmed et al. 2015; Khan et al. 2020).

Various removal efficiencies of emerging contaminants by commercial activated carbons have been published, due to the intrinsic physical and chemical properties of carbons, and the different experimental conditions (pH, contact time, type of water) used (Adams et al. 2002; Westerhoff et al. 2005; Snyder et al. 2007; Foo and Hameed 2010; Rivera-Utrilla et al. 2013; Nam et al. 2014). Interestingly, some hydrophilic pharmaceuticals and personal care products were successfully trapped *via* adsorption, despite of their low hydrophobicities. In fact, the mechanisms of adsorption are not yet fully elucidated (Rivera-Utrilla et al. 2013; Nam et al. 2014; Jeirani et al. 2017).

For example, Adams et al. (2002) showed that pharmaceuticals such as sulfamethazine, trimethoprim, and carbatox were effectively removed (81–98%) from water using powdered activated carbon. In contrast, Westerhoff et al. (2005) reported the wide ranges of removals (20–69%) for the pollutants such as acetaminophen, caffeine, diclofenac, naproxen, sulfamethoxazole, and atrazine by applying powdered activated carbon. Snyder et al. (2007) also demonstrated that 30–78% of pharmaceuticals were removed from river water samples using powdered activated carbon.

Yu et al. (2009) reported a comprehensive study regarding the adsorption of two pharmaceuticals (naproxen and carbamazepine) and an endocrine disrupting (nonylphenol) compound from a full-scale drinking water treatment plant by activated carbon in granular or powder form. The results showed that activated carbon form affected pollutant adsorption to carbon. Powder carbon would be most appropriate for achieving 90% of pharmaceuticals removal at a concentration of 500 ng/L, whereas granular carbon would be more suitable for nonylphenol. The authors explained this result by the fact that nonylphenol was much less impacted by fouling than the other two molecules.

Mailler et al. (2016) tested the use of micro-grain activated carbon (CarboPlus® technology) in a fluidized bed to remove pharmaceuticals, hormones and personal care products contained in treated wastewater from a municipal wastewater treatment plant (Seine Centre Paris, Colombes, France; 240,000 m^3/day corresponding to 9000,000 population equivalent). Large-scale experiments using a 5 m high reactor with a surface of 4 m^2 (10 g or 20 g of carbon per m^3, flow rate 1400 m^3/day, contact time between 10 and 20 min) have shown that a carbon-based configuration as tertiary treatment substantially improved the overall quality of the discharge waters. Indeed, micro-grain activated carbons can further reduce the residual pollution still present in biologically treated waters: reduction of biological oxygen demand (38–45%), chemical oxygen demand (21–48%), and dissolved organic carbon (13–44%). Besides, removal of ammonium, nitrite (total elimination) and total suspended solids has also been detected. On the other hand, carbon filters were most effective in removing pharmaceutical compounds (52 molecules) and hormones (10 molecules) and other emerging substances (57 molecules) such as alkylphenols, bisphenol A, parabens, pesticides (23 molecules) and sweeteners (50 to >90%). Thirteen campaigns of analytical monitoring have been realized. Pharmaceuticals had a good affinity for micro-grain activated carbon and high (>60%) or very high (>80%) removals were observed for most of the quantified compounds (22 substances of the 32 quantified): for example, atenolol (concentration 448 ± 400 ng/L; reduction of 92–97%), carbamazepine (74 ± 65 ng/L; 80–94%), ciprofloxacin (184 ± 95 ng/L; 75–95%), diclofenac (1120 ± 1400 ng/L; 71–97%), oxazepam (239 ± 110 ng/L; 74–91%) and sulfamethoxazole (1430 ± 1450 ng/L; 56–83%). The ten remaining substances that were less eliminated (25–75%) include for example acetaminophen, ibuprofen and iothalamic acid. Personal care products, alkylphenols, artificial sweeteners, benzotriazole, bisphenol A, pesticides and perfluorinated acids have also a good affinity for micro-grain activated carbon, while phthalates are not or poorly eliminated. Micro-grain activated carbon allowed obtaining performances comparable to conventional powdered activated carbon at a same fresh activated carbon dose, even if slightly higher removals are observed with powdered activated carbon for several compounds. The differences are explained by the nature of micro-grain activated carbon, which is reactivated, and more likely by the injection of $FeCl_3$ with powdered activated carbon. However, micro-grain activated carbon removes nitrites and total suspended solids, contrarily to powdered activated carbon. In addition, the micro-grain activated carbon configuration leads to several significant operational advantages over powdered activated carbon for a similar cost (≈ 1000–1200 €/ton), such as the ease of operation, the non-necessity to use $FeCl_3$ and polymer and the reactivability of the adsorbent (no waste to handle). Mailler et al. (2016) concluded that micro-grain activated carbon was more suited than powdered activated carbon for wastewater treatment at large-scale applications.

Nam et al. (2014), studying the adsorption of pharmaceuticals, pesticides and endocrine disruptors, also reported that in addition to carbon form, carbon dose and contact time affected the performance. Increased dosage of activated carbon and increased contact time allowed greater opportunity for the adsorbent to interact with target emerging contaminants, and enhanced adsorption removal was attained. Modifying the adsorbent dosage and contact time can maximize the removal of micropollutants. However, a cost-effectiveness analysis is necessary before implementing these solutions in field facilities. In addition, the adsorption of hydrophilic contaminants, such as caffeine, acetaminophen, sulfamethoxazole, and sulfamethazine, was significantly affected by the pH, whereas low temperature decreased the adsorption of hydrophobic pollutants such as naproxen, diclofenac, 2,4-dichlorophenoxyacetic acid, triclocarban, and atrazine. For example, removal of acetaminophen and sulfamethoxazole changed significantly due to electrostatic interactions between the adsorbent surface and the ionic species of these substances. The charge state of ionizable pollutants can affect micropollutants at certain pH levels. Low temperature can decrease the diffusion of lipophilic pollutants during the hydrophobic interaction with the adsorbent. A decrease in adsorption removal in surface water samples was observed and this decrease was more significant for hydrophobic than hydrophilic compounds. The decline in the adsorption capacity in surface water samples was caused by the competitive inhibition of dissolved organic matter with pollutants onto activated carbon. Nam et al. (2014) pointed out the fact that it was important to consider the effects of dissolved organic matter when treating pollutants in a water treatment plant.

Katsigiannis et al. (2015), studying the removal of emerging contaminants from water by granular activated carbon columns, demonstrated that the process removed endocrine disrupters (bisphenol A, triclosan) more efficiently than pharmaceuticals (ibuprofen, naproxen, ketoprofen) at concentrations up to 2 μg/L. In all experiments, the performance was enhanced by increasing the depth of the carbon bed. Among the target compounds, triclosan had the highest removal efficiency while ibuprofen was the least effectively removed. At a surface velocity of 3.1 m/h, removal rates after 5 days of continuous operation were 74.7% for bisphenol A, 86.7% for triclosan, 57.4% for ibuprofen, 65.6% for naproxen and 61.4% for ketoprofen for a bed depth of 8 cm, while virtually complete removal was achieved for all target compounds at a bed depth of 16 cm. The authors explained their results by correlating with the pKa and the log K_{ow} values of the target substances. During the experiments, microbiological activity was also observed, which stabilized the breakthrough curves that significantly extended the column's service life. Katsigiannis et al. (2015) concluded that activated carbon in the form of granular activated carbon columns can provide for the effective removal of target compounds in a municipal wastewater treatment plant.

Patiño et al. (2015) proposed the adsorption of emerging pollutants (1,8-dichlorooctane, nalidixic acid and 2-(4-methylphenoxy)ethanol) on functionalized multiwall carbon nanotubes. Recently, the use of carbon nanotubes has gained interest for the removal of different pollutants in the aqueous streams. These materials are a new member in the carbon family, including single walled and multi-walled nanotubes distinguished by their number of layers. They had exceptional mechanical properties, excellent electronic properties, large surface specific area, and their structure can be further tuned locally by oxidation treatment or surfactant treatment. Indeed, carbon nanotubes allow the surface modification in order to maximize the selectivity of adsorption through families of compounds, helping to improve the desorption behavior. When combined with membrane filtration, these innovative adsorbents demonstrated excellent removal of pharmaceuticals and personal care products with removals up to 95% (Kurwadkar et al. 2019). Other examples of results obtained using carbon nanotubes are described in the review published by Khan et al. (2020). Carbon nanotubes are considered to be promising adsorbents for water and wastewater treatment, although their high price is an important parameter to consider and their adsorption capacity depends strongly on both the hydrophobicity of the adsorbates and the morphology of the materials used. The materials can also be used in photocatalytic degradation processes in combination with a filtration step for the removal of endocrine disruptors (Patiño et al. 2015; Kurwadkar et al. 2019; Khan et al. 2020).

How to reduce the cost of adsorbents and improve their adsorption performance, while at the same time seeking environmentally friendly materials, has been a preoccupation of the research community since the 2000s. The development of cheaper, effective and novel materials for pollutant removal is currently an active field of research, as shown by the numerous studies published every year. Research is divided into two directions: the use of natural, cheap and abundant non-conventional materials in raw or modified forms and the development of conventional/commercial and new (synthetic) materials.

Several various studies have been carried out to replace active carbon by other adsorbent/biosorbent materials (Aksu 2005; Crini 2005, 2006, 2010, 2015; Ahmaruzzaman 2008; Vijayaraghavan and Yun 2008; Crini and Badot 2010; Ali 2012; Fomina and Gadd 2014; Kyzas and Kostoglou 2014; Couto et al. 2015; Ferreira et al. 2015). Commercial materials adopted at industrial scale for potable water treatment, effluent treatment and decolorizing applications include zeolites, activated alumina, and silica gels (Crini and Lichtfouse 2018a, b; Crini et al. 2019). Other conventional materials are commercial ion-exchange resins and synthetic organic resins. Non-conventional adsorbents/sorbents include clays (e.g. bentonite), siliceous materials (e.g. perlite, alunite), waste materials from agriculture (e.g. rice husk, biochar) or forest industries (e.g. bark, sawdust), by-products from industry (e.g. red mud, sludge), coal derived from non-conventional resources, biosorbents (e.g. peat, chitosan, alginate, cyclodextrin polymers), aquatic macrophytes, and biomass (Adriano et al. 2005; Crini 2005, 2006; Bekçi et al. 2006, 2007; Kang et al. 2010; Braga et al. 2011; Liu et al. 2012a, b; Lian et al. 2014; Xie et al. 2014; Freitas et al. 2017; Stofela et al. 2017; Portinho et al. 2017; Maia et al. 2017, 2019; de Andrade et al. 2018; de Souza et al. 2018, 2019; Osei et al. 2019; Fenyvesi et al. 2020; Macedo et al. 2020).

Which is the best adsorbent to replace activated carbon? There is no direct answer to this question because each adsorbent has advantages and drawbacks (Morin-Crini and Crini 2017; de Andrade et al. 2018). It is important to note that all non-conventional materials are basically at the laboratory stage in spite of unquestionable progress. Nevertheless, they will undoubtedly be at the centre of some extremely profitable commercial activities in the future (Morin-Crini and Crini 2017; de Andrade et al. 2018). Examples of such materials are described below.

1.4.2 Removal of Hazardous Contaminants Using Low-Cost Clay-Based Adsorbents

Clays are natural well-known minerals having layered structures with large surface area, high porosity, and high chemical and mechanical stability (Beall 2003; Crini 2006; Bhattacharyya and Gupta 2008; Crini 2010; Lofrano 2012; Gupta and Bhattacharyya 2014; Zhu et al. 2016). In addition, these materials are low-cost and abundant on most continents and they are studied as alternatives to activated carbons (Mercurio et al. 2019). Low-cost is naturally an important advantage of clays as adsorbents, e.g. the cost of montmorillonite can be up to 20 times cheaper than activated carbons (de Andrade et al. 2018). The performance of a clay material depends mainly on its chemical nature and pore structure. Clays are considered as strong candidates for ion-exchange and as host materials with a strong capacity to adsorb neutral and charged species (Bhattacharyya and Gupta 2008; Crini 2006). In general, pollutant removal efficiencies by clays are comparable or even higher than by commercial carbons. So, their use in adsorption-oriented processes for water purification and wastewater decontamination has become commonplace in industry today. The first recognition of their ability to sorb pesticides such as 2,4-dichlorophenoxyacetic acid (herbicide 2,4-D) from aqueous solutions was established in the 1970s (Beall 2003). Other practical applications of clays include purification of air, separation, sterilization and disinfection.

Currently, there is great interest in the adsorptive processes using clays that are considered promising and effective in the environmental remediation of emerging contaminants. As effective adsorbents, clays interact with recalcitrant dyes used in cosmetics (Almeida et al. 2009; Rehman et al. 2013), pharmaceuticals (Maia et al. 2017) such as antibiotics, antihypertensives, anti-inflammatory drugs, beta-blockers, and other psychoactive substances (caffeine), and pesticides (Grundgeiger et al. 2015).