Organic Micropollutant Removal by Biological Activated Carbon Filtration: A Review

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The Urban Water Security Research Alliance (UWSRA) is a $50 million partnership over five years between the Queensland Government, CSIRO's Water for a Healthy Country Flagship, Griffith University and The University of Queensland. The Alliance has been formed to address South-East Queensland's emerging urban water issues with a focus on water security and recycling. The program will bring new research capacity to South East Queensland tailored to tackling existing and anticipated future issues to inform the implementation of the Water Strategy.

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Cover Photograph:

Description: From left to right; Pilot scale Biological activated carbon (BAC) filtration columns installed in Caboolture reclamation plant, Granular activated carbon (GAC) on a laboratory bench, and Scanning Electron Microscopy image of a BAC grain.
Photographer: Maxime Rattier
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FOREWORD

Water is fundamental to our quality of life, to economic growth and to the environment. With its booming economy and growing population, Australia's South East Queensland (SEQ) region faces increasing pressure on its water resources. These pressures are compounded by the impact of climate variability and accelerating climate change.

The Urban Water Security Research Alliance, through targeted, multidisciplinary research initiatives, has been formed to address the region's emerging urban water issues.

As the largest regionally focused urban water research program in Australia, the Alliance is focused on water security and recycling, but will align research where appropriate with other water research programs such as those of other SEQ water agencies, CSIRO's Water for a Healthy Country National Research Flagship, Water Quality Research Australia, eWater CRC and the Water Services Association of Australia (WSAA).

The Alliance is a partnership between the Queensland Government, CSIRO's Water for a Healthy Country National Research Flagship, The University of Queensland and Griffith University. It brings new research capacity to SEQ, tailored to tackling existing and anticipated future risks, assumptions and uncertainties facing water supply strategy. It is a $50 million partnership over five years.

Alliance research is examining fundamental issues necessary to deliver the region's water needs, including:

- ensuring the reliability and safety of recycled water systems.
- advising on infrastructure and technology for the recycling of wastewater and stormwater.
- building scientific knowledge into the management of health and safety risks in the water supply system.
- increasing community confidence in the future of water supply.

This report is part of a series summarising the output from the Urban Water Security Research Alliance. All reports and additional information about the Alliance can be found at http://www.urbanwateralliance.org.au/about.html.

C. Davis

Chris Davis
Chair, Urban Water Security Research Alliance

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EXECUTIVE SUMMARY

Wastewater reuse is being increasingly seen as the main long term strategy for conservation of limited freshwater resources and also as a means of safeguarding the aquatic environment due to contaminants present in wastewater. One of the common concerns regarding human and environmental health is the presence of components of organic matter originating from wastewater treatment plant (WWTP) effluents (EfOM). Of particular concern are the so called "emerging contaminants" which are present in the environment and could be causing adverse ecological and health impacts, even at very low concentrations (ng L^{-1} range). Pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), plasticisers (e.g. bisphenol-A), flame-retardants, fuel additives and other industrial organic pollutants have been found in increasing concentrations in ground- and surface water.

Conventional WWTPs have been designed for the removal of bulk substances (primarily organic matter and the nutrients nitrogen and phosphorous). Organic micropollutants are entirely different, represent a minor part of the organic load and have individual behaviour through treatments depending on their properties. The removal of organic compounds during conventional activated sludge treatment and membrane bioreactors has been shown to be highly variable (Petrovic et al., 2009). Depending mainly on their sorption behaviour and biodegradability, chemicals bind to matter or can be transformed and eventually mineralised. Some micropollutants are still found in trace amounts in finished drinking water (Snyder et al., 2003a). In this context, special attention is given to control involving the application of advanced technologies to minimise the environmental release of a large number of micropollutants with very different properties in a broad range of water matrices.

Investigations have to focus on the effective treatment and, if possible, degradation of existing contaminants. Currently available technologies for the efficient removal of micropollutants from wastewater are based on membrane filtration, activated carbon, oxidation, managed aquifer recharge, and slow sand filtration. Persistent micropollutants can be removed by membrane filtration or activated carbon adsorption, however, depending on operation time, the adsorption or retention capacity of both approaches decreases due to interference with EfOM (Effluent Organic Matter). Biofouling can lead to clogging of filters and the need for cleaning and replacement in the long term. For their successful application, both approaches need improved regeneration strategies, which avoid impairing their performance and redischarging micropollutants into the environment.

After presenting some of the environmental and sanitary impacts associated with micropollutants released in WWTPs effluents, this document first reviews the physical process of adsorption by activated carbon. Granular Activated Carbon (GAC) filters have been used for decades to remove fractions of Dissolved Organic Carbon (DOC), various kinds of micropollutant and disinfectant by-products from water by adsorption. Practically, the efficiency of activated carbon will mainly rely on the accessibility of compounds to the adsorption sites on the media (pore size distribution), on the heteroatom content and the properties of the adsorbates. Thus, the influent micropollutant and DOC concentrations, contact time with the GAC, and type of GAC are major parameters influencing the adsorption. With the presence of large amount of DOC (dissolved organic carbon) compared to micropollutants, the adsorption of organic compounds is rapidly limited after feedwater starts flowing through the media (approximately 5000 bed volumes). As the adsorption capacity decreases, microbial colonisation can grow into a significant biofilm.

Biological activity, particularly high on activated carbon, starts after a few weeks of filtration, depending on the feedwater, and is commonly expected to extend the lifetime of GAC filters now termed biologically active carbon (BAC) filters. The second part of this review aims to describe the important factors responsible for the performance of BAC used in water purification. An analysis of the composition and activity within BAC filters as a function of service lifetime is given to better understand several physico–chemical and microbiological characteristics of the BAC grains. Microbial biomass is capable of biodegrading waterborne nutrients and fractions of Effluent Organic Matter such as Assimilable Organic Carbon which is readily metabolised by the biomass present in the BAC filter. When contaminants are removed by BAC, two main parallel mechanisms are involved: adsorption due to the presence of adsorption sites on the activated carbon, and biodegradation due to microbial activity developing in the crevices of the media. During BAC filtration, the participation of each mechanism evolves as the filter becomes exhausted and biodegradation is the most significant mechanism for DOC removal after exhaustion of the adsorption capacity. Work carried out at pilot plant scale comparing BAC and sand biofilters showed that BAC has good potential for the removal of DOC (35 to 60%), PPCPs (>90%) and toxicity (baseline-TEQ: 28 to 68%) even without pre-ozonation, whereas biofilms on sand beds with comparable dimensioning showed limited improvement of effluent quality (Reungoat et al., 2011). Clear evidence on the mechanism by which biological activity enhances MP (micropollutant) removal by GAC is currently lacking.

Moreover, the ability of the biofilm to remove and biodegrade waterborne organic substances and pollutants will be reviewed, with specific reference to other industrial biofiltration techniques such as slow sand filtration (SSF), river bank filtration (RBF) or soil aquifer treatment (SAT). Biodegradation is well known to play a role in the DOC removal achieved by sand or soil filtration techniques. It is also noteworthy that basic knowledge about the behaviour and fate of micropollutants in the environment is lacking. The use of bacteria supported on activated carbon allows combining the capabilities of both to retain and/or degrade organic compounds and, eventually, a synergistic effect is expected between support and biofilm (Quintelas et al., 2010). According to Herzberg et al. (2003) an adsorbing biofilm carrier, like GAC, can be the source of an extra flux of pollutant to the biofilm thanks to the existence of some biofilm-free areas. This double flux can improve the performance of BAC reactor as compared to a non-adsorbing carrier medium. However, to date, the mechanisms implied in the removal of organic micropollutants by BAC filters are still largely unknown and most filters have been designed empirically by anticipating the adsorption capacity decay due to continuous DOC loading. Further investigation of removal mechanisms occurring at the surface of BAC media is guaranteed to provide better assessment of the performance capability of such filters.

1. WASTEWATER REUSE

1.1 Is it Necessary?

The production and supply of potable water and the disposal of wastewater are among the major challenges of the 21st century. With growing water demands, access problems to safe and clean water for consumption are expected to increase across the world in the coming decades, even in regions considered as water-rich (Shannon et al., 2008). There is growing evidence that global warming will exacerbate these adverse impacts in the future, with more frequent and severe droughts expected across areas of the world. The more conventional methods of securing water supply, such as reservoirs, inter-basin transfers and desalination, all have irremediable negative environmental impacts (Collins et al., 2009). Treated wastewater effluent provides a dependable water supply relatively unaffected by periods of drought or low rainfall, suitable for discharge to surface waters, fire suppression, irrigation, some industrial applications and further potabilisation treatment. Even if these methods do not reduce water use, they have the potential to decrease abstraction from conventional sources. However, although advanced wastewater treatment will undoubtedly reduce the discharges of micropollutants, it will also inevitably result in large financial costs, as well as environmentally undesirable increases in energy consumption and CO_2 emissions.

1.2 Water Reuse Overview

To capture water directly from non-traditional sources such as industrial or municipal wastewaters and restore it to very high quality at an affordable cost is challenging. Wastewater contains a wide variety of contaminants and pathogens, and has a very high loading of organic matter, which must be removed or transformed to harmless compounds. The level of treatment required for each water type prior to recycling depends on the reuse application intended and the degree of contamination from faecal material, domestic and industrial chemicals and nutrients, both organic and inorganic.

Non-potable reuse is a large category encompassing various types of water usages, and saving large amounts of potable water for drinking, since less potable water will be used for non-potable uses. Indirect Potable Reuse involves feeding treated reclaimed water into existing, potable water storage (surface reservoir, aquifer system, river or lake) prior to further treatment and distribution, providing an additional water source to supplement main water supplies. The receiving water source provides an additional environmental barrier for pathogens and chemical contaminants. In the city of Beijing, for example, 50% of the drinking water supply is drawn from urban aquifers. About 30 to 60 % of the drinking water produced originates from treated or untreated wastewater (Schirmer and Schirmer, 2008).

In direct potable reuse the effluent of a wastewater treatment plant is routed directly to the intake of a drinking-water treatment plant. The option of direct potable reuse is the most technically demanding and societally contentious. Nevertheless, a well known example of direct potable reuse is the Goreangab Water Reclamation Plant in Namibia which has been using water purification for drinking purposes since 1968, providing today 35% of the daily requirement of the city of Windhoek.

1.3 Conventional WWTP Effluent Quality

1.3.1 Effluent Organic Matter

Large amounts of water to be recycled are typically derived from domestic wastewaters that have been treated by biological processes first. As such, this water will contain organic compounds from natural and anthropogenic sources, which are resistant to biological degradation. The elimination of organic matter by biological treatment is 96% for the bulk and 90% for the soluble fraction (Dignac et al., 2000). The hydrophobic fraction, such as humic substances, is more recalcitrant to biodegradation because of its size and structure (Krasner et al., 2009). In addition to influent refractory substrates not assimilated by bacteria during wastewater treatment, the EfOM from biological WWTPs is composed of degradation products and soluble microbial products (SMPs).

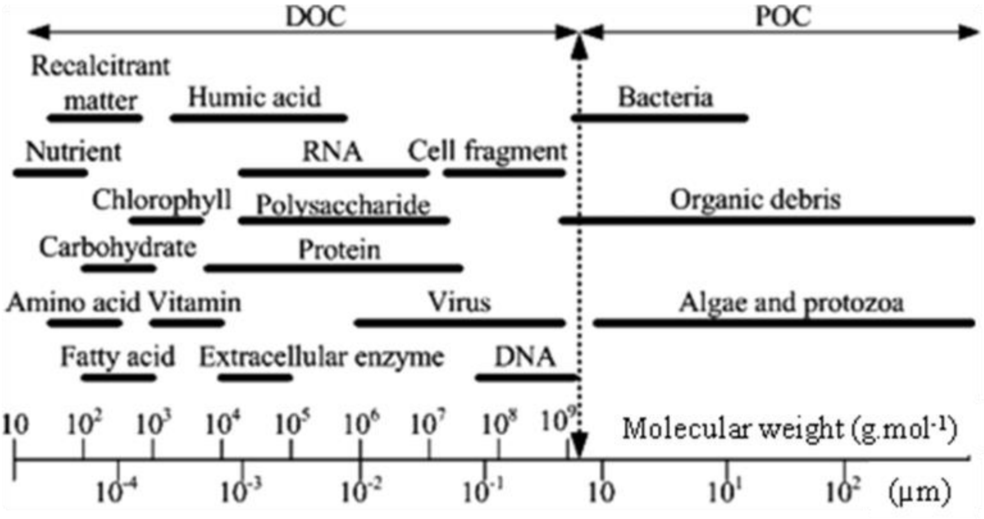

Figure 1: Organic Components in Traditional Wastewater Treatment Plant Effluent. Adapted from Shon et al. (2006).

Total organic carbon (TOC) includes particulate and dissolved substances while the DOC is measured in filtered samples and represents the dissolved component only. As particulates are easily removed by the coagulation/flocculation process it is DOC that is of most interest when investigating improved organic matter removal from water. The usefulness of DOC alone to describe the organic content of water is, however, limited and other supplementary analytical techniques offer more information on organic carbon character (Chow, 2003). Parameters such as the molecular weight, concentrations of biodegradable and assimilable fractions, disinfection by-product formation potential and hydrophobic/hydrophilic character are of importance to optimise the choice for the treatment of DOM. Although fluorescence measurements are limited to measuring fluorophores, the observed changes in the Excitation−Emission Matrix (EEM) fluorescence spectra can give insights into the transformations of organic matter during treatments.

The consequences of the presence of EfOM in recycled water include:

- loss of residual disinfection in recycled water systems
- interference with treatment processes for trace chemical removal
- formation of undesirable disinfection by-products
- undesirable bacterial growth and biofilm formation in water distribution systems
- anaerobic conditions in water transport systems.

Bacterial regrowth in drinking water distribution systems is the multiplication of viable bacteria downstream from the treatment plant. Chlorination is not sustainably effective in controlling regrowth (van der Kooij, 1992). The inactivation by chlorine is not sustainable as the compound disappears during distribution and has a limited effect on attached bacteria (Charnock and Kjønnø, 2000). Biodegradable Dissolved Organic Carbon (BDOC) is often considered the limiting nutrient for bacterial growth in water distribution systems as it constitutes the fraction of DOC utilised by microbes for growth and reproduction. In recent years, considerable effort has been made in drinking water treatment to develop methods that remove organic matter from water. Reducing organic carbon concentrations in water will have multiple effects, including the limitation of biofilm development and reducing components directly responsible for disinfectant decay in the distribution system, as well as reducing the precursors of disinfection by-products formation (CRC, 2005a). This contributes to improved plant control and better water quality for consumers (CRC, 2005b).

1.3.2 Organic Micropollutants

1.3.2.1 Sources in the Environment

The presence of organic micropollutants in the environment, and their potential to induce adverse biological effects, have been known for many years (Aherne and Briggs, 1989, Tabak and Bunch, 1970). In recent last decades, the drinking water industry has become increasingly concerned about the presence of these substances in water sources used for drinking water supply. Attention was first on pesticides but shifted towards other organic micropollutants which were found in increasing concentrations in ground- and surface water. The technical difficulties of controlling the release of micropollutants into the urban aquatic environment arise from incomplete removal in WWTPs and the subsurface leakage of sewers (Schirmer and Schirmer, 2008). However, there are other sources which are probably also of quantitative importance, because they mostly reach the aquatic environment without treatment: agriculture, construction materials, weed and pest control chemicals. Substances such as endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) represent a broad and diverse group of biologically active compounds that are used in large quantities in human and veterinary medicine around the world. The potential risk associated with the presence of low levels of pharmaceuticals in aquatic environments is currently under debate.

1.3.2.2 Effects

Research continues to clarify the toxicological significance of these trace EDCs/PPCPs in the environment and drinking water. The concerns of consumers have caused increased regulatory focus on this issue, even though the EDCs/PPCPs appear at reportedly low levels (Snyder et al., 2003a). Pharmaceuticals are, by design, biologically active compounds (with the exception of contrast agents, which are diagnostic compounds rather than pharmaceuticals). Their potential to affect a range of physiological processes in a large variety of non-target organisms is a concern. It has been shown that some pharmaceuticals may influence both the structure and the function of algal communities in stream ecosystems receiving treated sewage effluents (Wilson et al., 2003) e.g. specific inhibition of photosynthesis in algae caused by β-blockers (Escher et al., 2006). Estrogens in the environment have been implicated in adverse health effects in both animals and humans for some years (Fent et al., 2006, Lai et al., 2002), and there is increasing evidence that other pharmaceutical compounds may also cause harm to overall ecosystem health (Filby et al., 2010). The example of the anti-inflammatory drug diclofenac, which was shown to cause the drastic falls in vulture populations in the Indian subcontinent (Oaks et al., 2004) demonstrates that pharmaceuticals can cause problems. A major concern also is the development of bacterial resistance (creation of "Super Bugs") from the release of antibiotics in the environment (Richardson, 2009). Others are known (or suspected) carcinogens and ingestion of these substances, even at very low concentrations, might be harmful in the long term. The question of mixture toxicity has recently attracted more and more interest and additive effect are to be expected from mixtures of EDCs (Kümmerer, 2009, Pomati et al., 2006). The simultaneous low-level presence of several compounds might lead to an increase of the environmentally available dose for non-targeted organisms (Basile et al., 2011). Mixtures of EDCs and PPCPs at nanogram per litre levels have the potential to induce adverse effects in human cell lines (Pomati et al., 2006). Moreover, emerging contaminants such as those mentioned above do not necessarily need to be persistent to be dangerous because they are introduced continuously into the environment (Barceló, 2003, Klamerth et al., 2010, Nakada et al., 2008).

1.3.2.3 Physicochemical Properties and Fate of the Micropollutants

Most of the EDCs and PPCPs are more polar than traditional contaminants and the majority have acidic or basic functional groups. These properties, coupled with occurrence at trace levels (i.e., <1 $\mu g\ L^{-1}$), create unique challenges for both analytical detection and removal processes (Snyder et al., 2003b). These trace contaminants are generally very diverse in chemical properties, and the degree to which they are removed by the commonly used biological activated sludge processes varies from nearly complete to very little (Ternes et al., 1999a). Physico-chemical properties of the compounds and the water treatment processes involved are important parameters. Both biodegradation and sorption are components of the natural attenuation process, during which parent compounds are lost from the aqueous phase. It is difficult to separate the influence of biodegradation from that of sorption

(Lin et al., 2010). Adsorption to soil and sediment is the tendency of a chemical to bind to the material at the bottom layer of a water body (e.g., a river bed). This is significant because chemicals trapped at the bottom of a river bed generally do not contaminate the drinking water supply. Sorption is an important pathway for elimination of pharmaceuticals and depends mainly on the characteristics of the target particles and on the extent of neutral and ionic species present. The log Kow (concentration ratio at equilibrium of an organic compound partitioned between octanol and water) gives an indication of the adsorption propensity of each compound. For example, estrogens are polar and hydrophilic in nature, suggesting low adsorption, but they are generally well biodegradable (Koh et al., 2008). The following classification was proposed by Jones et al. (2005a) to assess the sorption potential for organic contaminants:

- log Kow < 2.5 Low sorption potential
- 2.5< log Kow < 4.0 Medium sorption potential
- log Kow > 4.0 High sorption potential

These properties are also an important factor from the analytical point of view, since they largely determine the solvents and sorbents for extraction or analytical techniques for their determination. Still, in most laboratories, detection of EDCs is not an easy task because of the trace levels (micro- or nanogram per litre or even less) of these compounds present in most natural waters and wastewaters.

While numerous compounds have been reported to preferentially adsorb onto suspended solids, many are sufficiently soluble to be amenable to biotransformation and bioconcentration (Jones et al., 2007a). Low-level exposure to biodegradable EDCs is also a problem, posed by the fact that biodegradation by-products might be even more dangerous than the parental compounds once discharged into recipient water bodies. The primary biodegradation compounds of alkyphenols are even more harmful than alkylphenols themselves (Basile et al., 2011). These latter compounds act as estrogen mimics, and even if their potency is orders of magnitude lower than that of natural estrogens, they are very persistent in the environment (Basile et al., 2011). Continuous discharge by WWTPs of non-biodegradable compounds and/or metabolites can result in a constant and relevant presence of hazardous xenobiotic chemicals. Complex issues for environmental health arise as a consequence of their potential to bioaccumulate (Jones et al., 2007a). Complete degradation or mineralisation, which can occur in water, soils and natural environment in general, is the conversion of the carbon in an organic chemical to carbon dioxide. This occurs when microorganisms break down a chemical to its elemental state (e.g., carbon dioxide, water and ammonia). Once the chemical is in its elemental state, it is no longer of concern.

Current human activities have a significant sanitary and environmental impact. The demand for fresh water is increasing with the growth in world population. To make wastewater reuse beneficial, conventional wastewater treatment plants (WWTPs) must be designed to remove effectively biodegradable organic matter and pathogens but also persistent organic micropollutants to minimise their sanitary and environmental impacts. Micropollutants are present at trace levels, having a broad range of chemical structures. Their physico-chemical properties are well known but their fate in the environment is currently under investigation.

2. MICROPOLLUTANT REMOVAL - WASTEWATER TREATMENT

2.1 Primary and Secondary Treatment

Primary treatment is a mechanical process that removes everything that floats or sinks in wastewater, as well as screening coarse material. Micropollutant removals obtained are low and mainly due to adsorption and depend largely on the hydrophobicity of the micropollutant, the suspended solids content and their subsequent settling. The retention time and surface loading are influential operational parameters. Lipophilic compounds such as fats, oils and greases can also adsorb a significant amount of hydrophobic compounds (Koh et al., 2008).

Biological wastewater treatment takes one of two general forms: suspended growth (biofloc) systems (e.g., activated sludge) and attached growth (biofilm) systems (e.g., trickling filters). Biological aerated (or anoxic) biofilters combine filtration with biological carbon reduction, nitrification or denitrification. Secondary treatment reduces overall concentrations of organic chemicals, including some human pharmaceuticals, hormones and fragrances (AGWR, 2008). The removal of pharmaceutical residues in secondary treatment processes includes four mechanisms: biotransformation, air stripping, phototransformation and sorption. Some substances may be subject to phototransformation but its impact is negligible, especially in activated sludge. Henry coefficients higher than 3×10^{-3} were required for the significant stripping of molecules in a bioreactor solution with fine bubble aeration (POSEIDON, 2006). Therefore, biotransformation and adsorption are the main mechanisms responsible for the significant removal of micropollutants in secondary treatment.

The removal of a substance does not necessarily indicate degradation, as sorption only causes a loss in detectability. Sorption mechanisms include ion exchange, complex formation with metal ions and polar hydrophilic interactions (Le-Minh et al., 2010) forming flocs subsequently disposed of as excess sludge. Whereas the fraction of these micropollutants sorbed onto biosolids was not often considered to be due to the lack of proper analytical methodologies (Radjenović et al., 2009), such data are however crucial for understanding of micropollutant behaviour during wastewater treatment and sludge disposal. Sorption may be responsible for a large removal of micropollutants from water but also has an impact on the spread of pharmaceuticals in the environment (particle bound transport) (Kümmerer, 2009). Sorption-desorption phenomena also influence the availability of compounds for microorganism degradation.

Transformation and biodegradation are thought to play a significant role in hormone removal, since some of the microorganisms present in biological WWTPs possess the potential to utilise steroid estrogens, amongst other micropollutants, as carbon sources for metabolism (Koh et al., 2008). While some compounds (ibuprofen, paracetamol, acetyl salicylic acid) are easily removed, others (carbamazepine, diclofenac) are barely affected by biological treatment in typical wastewater treatment (Onesios et al., 2009). Recalcitrant organic chemicals are of particular interest because these are resistant to biodegradation and are thus challenging to remove during standard activated sludge sewage treatment. However, removal only means that the parent compound of interest is no longer detectable by compound specific analysis. Additional molecules may be formed after the excretion of parent compounds and metabolites into the environment. This should be referred to as transformation. Many pharmaceuticals and their metabolites are further bio-transformed into transformation products by organisms such as bacteria and fungi, both in the environment and in water treatment facilities (Kümmerer, 2009).

The biological WWTP constitutes a first point where improved micropollutant removal can be aimed for at an affordable cost. Research and development have been done on the operation and design to improve the reduction in micropollutant content of WWTP effluents. Depending on operational conditions, biomass can function as partially or completely nitrifying. Advanced biological treatment may include denitrification, where nitrate is converted primarily to nitrogen gas. A recent study in England showed particularly dramatic benefits of adding a biological step. Simply adding a short secondary treatment stage of fine bubble aeration to a domestic WWTP that previously had only primary settlement produced a sudden and sustained reversal in feminisation trends in fish downstream (McCann, 2004). The most rapid and complete degradation of pollutants present in the WWTPs is brought about under aerobic conditions through catabolic pathways (Moharikar et al., 2005). Little is known about the microorganisms that are responsible for the actual degradation of micropollutants in wastewater. Moreover, the population dynamics of such microorganisms depend greatly on the type of process i.e. trickling filter, activated sludge process, membrane bioreactors and enhanced biological process.

2.2 Nitrification and Denitrification

Nitrifying sludge was first reported to enhance transformation of the estrogen, 17α-ethinylestradiol (EE2) into metabolites devoid of estrogenic activity (Vader et al., 2000). For instance, it has previously been shown that WWTPs utilising both nitrification and denitrification treatment steps and/or high sludge ages (~15 days) exhibit better removal rates for EDCs and pharmaceuticals than those using standard operating conditions (Jones et al., 2007a). The reason for this is likely to be the role of co-metabolism and the presence of monooxygenase enzymes (Jones et al., 2007a). Ammonia oxidizing bacteria are a group of ubiquitous lithoautotrophic microorganisms that can express ammonia monooxygenase (AMO) enzyme to oxidize ammonia to nitrite. The primary goal of nitrification is to transform ammonia and organic nitrogen to nitrate, but increased levels of nitrification are usually accompanied by additional decrease in the biological oxygen demand and removal of the biodegradable fraction of DOC (Krasner et al., 2009). In addition to the ammonia oxidation, AMO enzymes are known to oxidise a wide range of aliphatic and aromatic hydrocarbons (Roh et al., 2009). Shi et al. (2004) reported that *Nitrosomonas europaea* was capable of degrading steroidal estrogens in wastewater. In a more recent study (Roh et al., 2009), *N. europaea* could degrade triclosan and bisphenol A, but not ibuprofen. The degradation was observed only in the absence of allylthiourea, an inhibitor for AMO, suggesting that the enzyme might be responsible for triclosan and bisphenol A degradation (Roh et al., 2009). Competitive inhibition of ammonia oxidation, shown by a decreased nitrite production, was observed when triclosan or bisphenol A was present (Roh et al., 2009). The authors suggested future studies to examine degradation kinetics for BPA, triclosan and estrogens.

Nitrification and denitrification play important roles in determining the quality of EfOM and disinfection by-product precursors (Krasner et al., 2009). In an analytical survey of 23 WWTPs that utilised a range of technologies, nitrification reduced the concentration (mg L^{-1} amounts) of hydrophobic and transphilic NOM to a limited extent, but resulted in a 36% better removal of the hydrophilic NOM compared to into nitrification. Denitrification is driven by the necessity of oxidising an organic electron donor and carbon source and, as a consequence, is useful to lower EfOM concentrations. Biological treatment that included nitrification appeared to remove a portion of the dissolved organic nitrogen that was reactive to form a nitrogenous class of DBPs, as well as non nitrogenous ones (Krasner et al., 2009). However, nitrification resulted in an EfOM with less DOC, but more reactivity to form trihalomethanes (THMs) per unit DOC (Krasner et al., 2009).

WWTPs employing nitrification and denitrification also exhibit significantly lower concentrations of drugs such as ibuprofen and naproxen in their effluent (Drewes et al., 2002). This is probably a consequence of the diverse bacterial compositions within a nitrifying and denitrifying system which may act synergistically and result in a greater degree of degradation being achieved (Jones et al., 2005b). For example, a compound may be partially biodegraded during nitrification, with the resulting product then degraded fully in the denitrification system. Despite the evidence that higher oxidation potentials in aerobic conditions should favour degradation, Drewes et al., (2001b) reported negligible removal of tri-iodinated benzene derivatives (X-ray contrast media) under aerobic conditions and significantly enhanced removal under anaerobic conditions. Different degradation pathways also seem to exist under aerobic and anoxic conditions. The contribution of nitrifying and denitrifying conditions to the removal of a broad range of PPCPs was investigated recently (Suarez et al., 2010). The process comprised two 2 L reactors inoculated with 1.5 year-old sludge, run at a hydraulic retention time (HRT) of 1 day in order to treat a synthetic feed containing an organic carbon source spiked with PPCPs at concentrations varying between 10 and 40 µg L^{-1}. Compounds could be classified according to their aerobic and anoxic biodegradability as illustrated in Table 1. The solid retention time (SRT) parameter was varied and two operational periods were distinguished: SRT >50 d and <50 d; SRT >20 d and <20 d for the nitrifying and anoxic system, respectively.

Table 1: Summary of PPCP transformations obtained in the nitrifying and denitrifying reactors. Adapted from Suarez et al. (2010).

Compound	Transformation		Influence	
	Aerobic	Anoxic	SRT	Sludge Characteristic
Galaxolide	++	+/++	No	No
Estrone:E1 + 17βestradiol: E2	++	+	Yes	No
Tonalide	++	+/++	No	No
Celestolide	++	+/++	No	No
Ibuprofen	++	--/+	No	Yes
Ethinylestradiol (EE2)	++	--/-	Yes	No
Fluoxetine	++	++	Yes	No
Roxithromycin	++	--	n.a.	No
Erythromycin	++	--/-	n.a.	No
Citalopram	+	-+	Yes	No
Naproxen	++	--	Yes	No
Diclofenac	--/+	--	No	Yes
Sulfamethoxazole	-	n.a.	n.a.	No
Diazepam	--	--	No	No
Trimethoprim	-	n.a.	n.a.	No
Carbamazepine	--	--	No	No

(--) <20%; (-) 20–40%; (-+) 40–60%; (+) 60–80%; (++) >80%; n.a. not analysed. The influence of SRT, and other characteristics of sludge (Sludge) on the transformation degree is indicated as (yes) or (no). Both reactors have been running at a HRT of 1 d.

Ten of the considered PPCPs were removed to a high degree (>85%) in the aerobic reactor, comprising hormones estrone, 17βestradiol and ethynilestradiol, the anti-inflammatory drugs ibuprofen and naproxen, the anti-depressant fluoxetine and two antibiotics: roxithromycin and erythromycin. Diclofenac, sulfamethoxazole, diazepam, trimethoprim and carbamazepine have not been significantly transformed (<25%) by biological treatment with neither nitrifying nor denitrifying bacteria (Suarez et al., 2010). The authors indicated that the behavior of diclofenac in the aerobic reactor was influenced to a greater extent by the biomass developed in the system than by the operation temperature and SRT. Indeed, results indicated that an initial adaptation period that coincides with the death and washout of heterotrophic bacteria (approximately 170 d) seemed to occur as removal of diclofenac increased from 0% to 25% (Suarez et al., 2010). Afterwards, a correlation between sludge concentration in the reactor and biological transformation of diclofenac was observed, reaching maximum removals of around 74% (Suarez et al., 2010).

In activated sludge systems, SRT appears to be an especially important factor in EDC removal. Several researchers have noted improved removal with increased SRT (Basile et al., 2011, Le-Minh et al., 2010, Suarez et al., 2010, Andersen et al., 2003, Göbel et al., 2007, Holbrook et al., 2002, Ternes et al., 1999b). A retention time of at least 10 to 12.5 days has been suggested as the time required for the growth of organisms that decompose E2 and E1 (Saino et al., 2004). Increasing SRTs were reported to enhance the removal of several pharmaceuticals during aerobic biological processes. The longer SRTs have been suggested to allow for the enrichment of slower growing bacterial species and therefore, to provide greater diversity of enzymes, some of which are capable of breaking down pharmaceutical compounds (Jones et al., 2005a, 2007). Similarly, prolongation of HRT is expected to provide sufficient reaction time for biotransformation to occur in order to reach maximum efficiency. However, it is difficult to generalise the expected relationship between HRT and pharmaceutical removal without accounting for the effect on biomass concentration. While resulting in only minimal improvement of elimination rates (Kümmerer, 2009), extending HRTs may cause high costs because of the necessity to enlarge the WWTPs. Rarely reported factors such as biomass concentration and diversity as well as substrate/biomass ratios have been suggested to be more important to explain the variations in micropollutant removal (Le-Minh et al., 2010).

2.3 Membrane Bioreactor

Among advanced treatments requiring major infrastructure interventions, membrane bioreactors (MBRs) systems might represent other viable options, as these processes maximise the use of existing facilities and allow the achievement of higher sludge retention times in smaller tank volumes. MBRs can offer the advantage of more flexibility to operate at higher SRTs with a smaller footprint. MBRs combine activated sludge treatment with the use of a microfiltration (MF) or ultrafiltration (UF) membrane to separate solids from liquid. This allows for very effective removal of both soluble and particulate biodegradable materials at higher loading rates. Sludge retention times usually exceeding 15 days ensure complete nitrification. However, the cost of building and operating an MBR is usually higher than for conventional wastewater treatment plants, and the membranes can be fouled over time. Steroid removal rates of greater than 90% were achieved in membrane bioreactors with nitrification and denitrification (SRT of 12-15 days) (Joss et al., 2004). The sludge originating from a membrane bioreactor (aged 30 days) showed significantly higher activity in batch experiments by a factor of 2-3 than in conventional activated sludge with a solids retention time of 11 days (Joss et al., 2004). While MF membranes themselves will not provide an enhanced degree of estrogen removal, it has been suggested that estrogen adsorption to particulate matter that is retained by the membrane would reduce estrogen concentration in the effluent. Indeed, since most organic micropollutants or steroid estrogens are small molecules, usually in the range from 150 to 500 Daltons, only those compounds that associate with particles or colloidal organic matter will be physically removed during MF and UF (Koh et al., 2008).

After release of emerging and newly identified chemicals into the environment, cleanup is extremely difficult. Conventional WWTPs are not designed for the removal of newly identified contaminants and removals vary dramatically. Secondary biological treatment of wastewater significantly reduces the concentrations of many of these substances.

Significant research and development is under way to establish methods and technologies to improve water and wastewater treatment. Anaerobic, nitrifying–denitrifying and methanogenic bacteria that carry out the detoxification of effluent contaminants have been discovered in various WWTPs. This suggests that operating conditions of conventional (aerobic) treatment plants can be optimised to manage biodegradation of some contaminants. The biodegradation of several compounds has been shown to require (a) a measurable increase of the sludge and hydraulic retention times (SRT and HRT,); (b) a reduced food-to-microorganism ratio (F/M) in the oxidation ditch; and (c) minor structural adjustments of existing plant configurations, possibly by the introduction of dedicated anoxic or anaerobic zones as in the case of EDCs.

3. ACTIVATED CARBON FILTRATION

3.1 Usage

Water treatment accounts for more than 70% of the liquid-phase activated carbon demand in industrialised countries (Rodríguez-Reinoso et al., 2001). Activated carbon is used in the treatment of drinking water to remove or control unpleasant taste and odour, and to remove organic compounds like chloroform and THMs. Activated carbon is also used in the treatment of municipal and industrial wastewater due to its ability to adsorb a wide variety of pollutants, including aromatic compounds, hydrocarbons, detergents, soluble dyes, chlorinated solvents, phenols, and hydroxyl derivatives. Adsorption processes do not add undesirable by-products to drinking water, but high adsorbent usage rates can be expected if activated carbon is employed to adsorb polar organic contaminants (Quinlivan et al., 2005). Activated carbon significantly reduces DOC in the treated water by binding the organic carbon compounds to adsorption sites in the activated carbon structure. TOC removal by GAC filtration in one Sydney system produced highly stable water (TOC = 0.1 to 1.2 mg L^{-1}) (Chandy and Angles, 2004). No biofilm development was detected in biofilm reactors after 60 days, owing to the free chlorine residual present in the system (approximately 1 mg L^{-1}) (Chandy and Angles, 2004). The results indicated that TOC removal increased the availability of chlorine to disinfect microorganisms, rather than removing organic carbon from developing biofilms, leading to their starvation. This was based on the observation that no biofilm development was detected in the chlorinated GAC treated water supplemented with biodegradable organic nutrients (Chandy and Angles, 2004). Activated carbon is employed by passing water to be treated through GAC filters or by dosing powdered activated carbon (PAC) to the water subsequently removed by sedimentation or filtration. The tendency is for an increasing proportion of the granular type because of its regeneration capability. The largest quantity of GAC is needed at the time of installation and about 10% per year of new carbon is required to sustain operation (Rodríguez-Reinoso et al., 2001).

3.2 Manufacture

Activated carbon is produced commercially from organic precursors rich in carbon (wood, nutshells, fruit pits, etc), peat, coal, lignite, pitch, coke, etc. There are two main manufacturing processes for the production of activated carbon: physical (also called thermal) activation and chemical activation. The degree of activation is measured by the carbon's specific surface area and adsorption capacity and is a function of time spent in the activation furnace: the longer the time, the greater the activation. Pore-size distribution in activated carbon depends on various factors, which include the raw material, type of activation, chemical agents/activating gases employed, temperature and time of reaction, and other operating parameters (Satya Sai and Krishnaiah, 2004). Activating gases also had considerable effects on the characteristics of activated carbon produced in a fluidised-bed reactor (Satya Sai and Krishnaiah, 2004).

3.3 Characterisation of the Adsorptive Properties

3.3.1 Pore Size Distribution

Following IUPAC recommendations (Rouquerol, Avnir et al. 1994), pore diameters can be classified as primary micropores (< 0.8 nm), secondary micropores (0.8-2 nm), mesopores (2-50 nm), and macropores (> 50 nm). The most common standard parameters for measuring carbon adsorptive capacity are: iodine number (I_N), which defines the micropore (<2 nm) of an activated carbon and therefore reflects its ability to adsorb small substances, and the molasses number, which defines the large pores (>50 nm) and is used as a relative guideline to measure the capacity of an activated carbon for larger molecules (Raposo et al., 2009). Another indicator of the adsorptive capacity of activated carbon is the methylene blue number (MB_N), reported in mg g^{-1} (approximate range 110–280 mg g^{-1}). This parameter is related to macro- and mesopores capacity of activated carbon. Physical gas adsorption is often preferred to accurately probe the small micropores, and an inert gas, mostly nitrogen, is adsorbed on the surface of a solid material. This occurs on the outer surface and on the surface of pores. Most widely known is the determination of the BET surface area by gas adsorption.

Adsorption isotherms of specific compounds, mainly iodine, methylene blue, phenol and nitrogen, are commonly used for the determination of the surface area and the analysis of the porosity.

Unfortunately, there is no standardised testing procedure to assess or compare the adsorptive capacity of GACs (Raposo et al., 2009), although three general methods are described in the literature. The first one involves adding a measured amount of activated carbon to a standard dye solution and is defined as the mg of dye adsorbed by one gram of carbon in equilibrium with e.g. a solution of dye with a concentration of 1 mg L^{-1}. The result is expressed in mg g^{-1}. The second one, less commonly used, involves the addition of a standard dye solution to a sample of activated carbon until no further discoloration occurs. The result is reported as mL g^{-1}. On the other hand, a lot of the research was reported in the literature in which the amount of dye removed from aqueous solution by unit of mass of activated carbon was obtained by using the traditional multi-point isotherm adsorption tests and applying a model to fit the experimental data.

Once the adsorption isotherm is obtained, it is analysed by an appropriate method to evaluate the so-called monolayer capacity, and from this the surface area is calculated if the area of one adsorbed molecule is known (Rodríguez-Reinoso et al., 2001). The BET method (Brunauer, Emmett, and Teller) is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. It is often stated that the BET surface areas obtained for primary micropores are not really meaningful in an absolute sense. In a study of the adsorption capacity of MB by 3 different GACs, Raposo et al. (2009) compared the adsorption capacities determined by the single point test and the traditional multi-point isotherm test. Varying MB/GAC mass ratios from 0.5 to 1 were tested by increasing the solution concentration and the maximum adsorptive capacity values were similar and statistically not different from those obtained with the single point tests (MB/GAC mass ratio of 0.75).

Frequently, those parameters are used to determine the degree of exhaustion of a carbon in use. However, this practice should be viewed with caution as chemical interactions with the already adsorbed compounds may affect the iodine or MB uptake, giving misleading results. Indeed, direct competition between molecules for the same adsorption sites was observed to occur (Pelekani and Snoeyink, 2000). Atrazine was preloaded using an initial concentration of 400–500 µg L^{-1} in contact with the fresh activated carbon fibres for seven days. It was found that the pesticide could be displaced from secondary micropores by MB solution (2.3 mg L^{-1}). Thus, the use of I_N or MB_N as a measure of the degree of exhaustion of a carbon bed can only be recommended if it has been shown to be free of chemical interactions with adsorbates and if an experimental correlation between dye adsorption and the degree of exhaustion has been determined for the particular application (Raposo et al., 2009).

3.3.2 Adsorption Isotherms

The adsorption isotherm expresses the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface at constant temperature or, in other words, the amount adsorbed per unit mass of adsorbent as a function of the equilibrium concentration in solution (Quintelas et al., 2010). Isotherms provide a significant amount of information about the adsorbent used and the interaction with the adsorbate in the system, including: i) assessment of the surface chemistry and fundamentals involved in the adsorption process; ii) estimates of the surface area, pore volume and pore size distribution; iii) efficiency profiles for carbons used in industrial processes. The shape of the isotherm is the first experimental tool to diagnose the nature of a specific adsorption phenomenon. There are several types of isotherm but those mainly found in carbon materials are depicted in Figure 2.

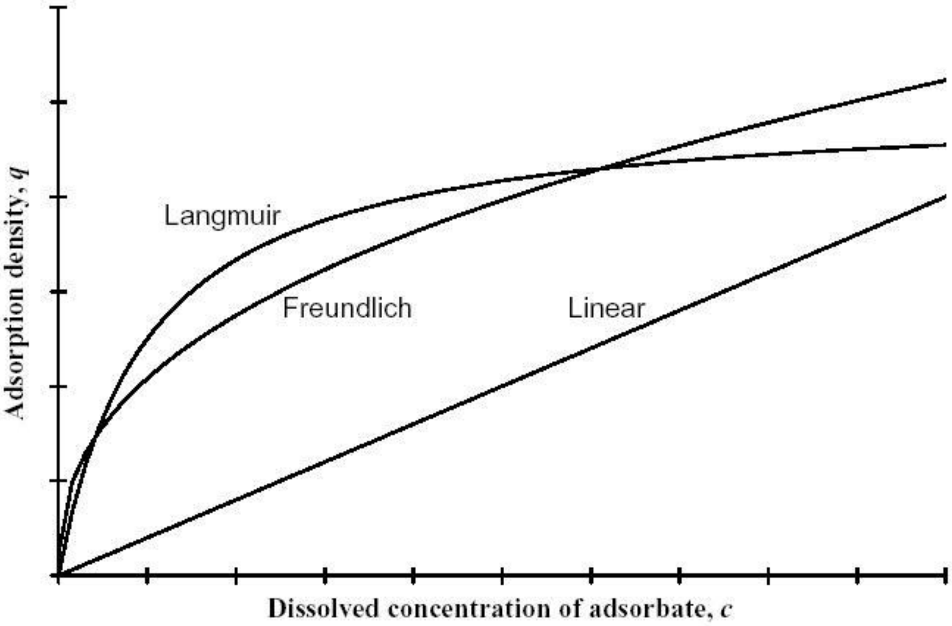

Figure 2: **The 3 most common generic adsorption isotherms found with activated carbon in aqueous solutions.**

Linear $q = k_{\text{lin}} c$

Langmuir $q = q_{\max} \dfrac{K_L c}{1 + K_L c}$

Freundlich $q = k_f c^n$

Where:

q: mass of compound sorbed per mass unit of GAC at the equilibrium (mg g^{-1})

c: concentration of compound in solution at equilibrium (mg L^{-1})

k_{lin}: linear adsorption constant

K_L: (L.mg^{-1}) Langmuir adsorption equilibrium constant

q_{max}: (mg g^{-1}) Maximum mass of compound sorbed per mass of GAC

k_f: Freundlich adsorption constant

n: intensity of adsorption

k_{lin}, K_L, q_{max}, k_f and n are constants, proportional to the adsorption capacity of the material, given for an adsorbate and adsorbent combination at a particular temperature. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into the sorption mechanism, the surface properties and the affinity of the sorbent (Gerente et al., 2007). Log-linear isotherms are not common in adsorption on carbons but are found in the initial part of all isotherms on homogeneous surfaces. The Langmuir type frequently occurs, even when the premises of the Langmuir theory are not satisfied. The Freundlich type, typical for heterogeneous surfaces, is perhaps the most common. High-affinity isotherms are characterised by a very steep initial rise, followed by a pseudo-plateau. Isotherms from solution may exhibit non-ideality, not only because of lateral interactions between adsorbed molecules but also because of non-ideality in the solution. Generally, a shift toward lower K values is equivalent to a lower sorption capacity.

3.3.3 Dynamic Column Studies

Batch equilibrium tests are often complemented by dynamic column studies to determine system size requirements, contact time and carbon usage rates. These parameters can be obtained from the breakthrough curves. To study these curves it is usual to apply a macro-approach method based on the mass transfer zone concept (MTZ). The basic principles of this concept are depicted in Figure 3.

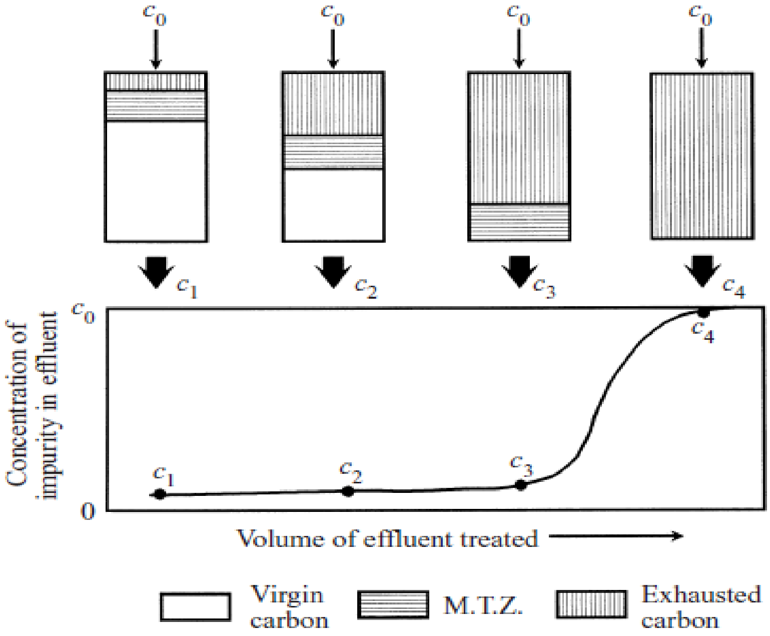

Figure 3: Progression of the adsorption front through the adsorber bed, and resulting breakthrough curve. Reprinted from Rodríguez-Reinoso et al. (2001) with permission from Elsevier.

As the volume of treated liquid increases, the impurity gradient moves towards the exit and eventually the impurity concentration equals that of the inlet as the carbon is exhausted. The section of the column where the mass transfer from the fluid to the carbon occurs is known as the mass transfer zone (MTZ). In other words, the MTZ is the distance between the layer of saturated exhausted carbon and the layer of virgin carbon. Figure 3 shows the various stages of adsorption through the carbon column, the movement of the MTZ, and the resulting outlet concentrations. Breakthrough occurs when the MTZ advances to the end of the bed. The height of this zone is a measure of the adsorption efficiency of the bed. The lower the height, the more efficient the carbon bed. The mass transfer rates for the adsorption of different compounds on carbon obey fundamental equations described by the relationship between C/C_0 and *t* in a system. Since the EfOM is present at much higher levels than the target compounds, the MTZ of organic matter moves toward the bottom of the filter more rapidly than the micropollutants (present at lower concentrations). Adsorbed NOM blocks pores and competes for adsorption sites. As a consequence the adsorption capacity, as measured by traditional methods (e.g. I_N and MB_N) is generally deemed to be exhausted after approximately 6 months or 5,000 bed volumes (Simpson, 2008, Yapsakli and Çeçen, 2010). Because the adsorption process occurs in a series of steps, the slowest step in the series is identified as the rate limiting step. In general, if physical adsorption is the principal mode of adsorption, one of the diffusion transport steps will be the rate limiting step, because the rate of physical adsorption is rapid. Where chemical adsorption is the principal mode of adsorption, the adsorption step has often been observed as to be rate limiting (Metclaff and Eddy, 2003). The theoretical adsorption capacity of the carbon for a particular contaminant can be determined by developing its adsorption isotherm.

3.4 Adsorption Mechanisms

Activated carbons exhibit a high degree of porosity and an extensive internal surface area. Because of the mainly nonpolar nature of carbonaceous adsorbents, they selectively adsorb nonpolar rather than polar substances. More specifically, a solute molecule contained in the bulk solution in the GAC column migrates from the bulk solution to a hypothetical film surrounding the GAC particle (i.e. the boundary layer) as shown in Figure 4. It then diffuses through the boundary layer to the outside surface of the GAC particle via film diffusion. Subsequently, the molecule is transported in the liquid phase within the pores of the GAC particle via pore diffusion, or along the wall of the pores by means of surface diffusion. Finally, the solute molecule, arriving at the adsorption site, attaches onto the carbon, a process that can be described by an adsorption isotherm. Mass transfer coefficients determined by dynamic column tests with virgin and preloaded GAC demonstrated that film diffusion primarily controls mass transfer on virgin and preloaded carbon (Yu et al., 2009).

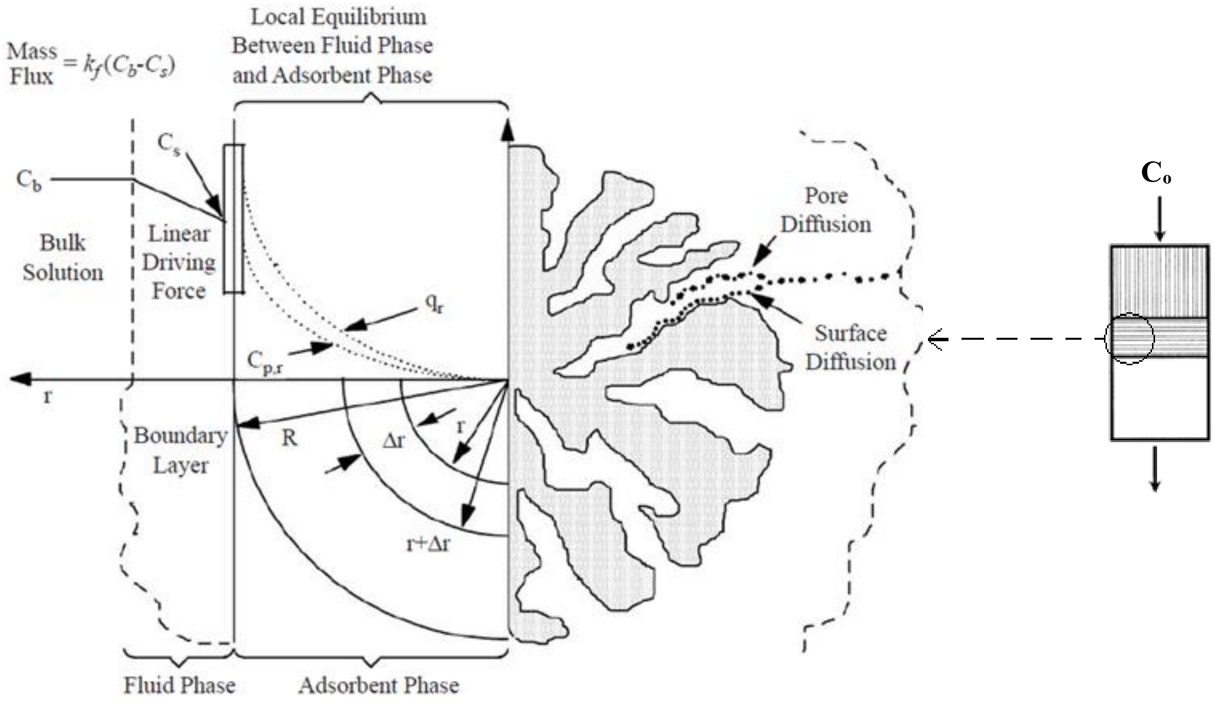

Figure 4: Mass transfer mechanisms in GAC adsorbents. Adapted from Jarvie et al. (2005).

The surface of activated carbon can bind molecules by physical forces of the van der Waals type and hydrogen bonding. Those non electrostatic interactions are always attractive. The hydrophobic effect also plays a major role in adsorption propensity. The hydrophobic effect will enhance the adsorption of a hydrophobic molecule but it is not responsible for the interactions between the AC surface and the molecule itself. For charged molecules the charge interactions are of great importance. Nevertheless, sorption efficiencies are always relying on the competition with other organic compounds encountered. Therefore, the organic compounds with higher logKow are expected to be better removed by activated carbon. Although users have traditionally considered the porosity and surface area to be the parameters defining the quality of activated carbon, it is now realised that the surface chemistry of the carbon plays an important role in the adsorptive properties. The surface chemistry of activated carbons essentially depends on their heteroatom content (oxygen, sulfur and nitrogen (Valix et al., 2006)), and mainly on their oxygen complex content (Moreno-Castilla, 2004). Heteroatoms are brought during the activation, providing charged groups with stronger valence forces in the carbon structure at which chemisorption may occur. These groups can reside within the carbon layers, forming heterocyclic rings, or bonded to edges and corners of the aromatic rings or carbon defect positions (Valix et al., 2006). As expected, the modification of the chemical nature (e.g. acidity or charge) of activated carbon will consequently have an effect on the adsorbent-adsorbate interactions and on the resulting adsorptive properties. Electrostatic interactions appear when the adsorbate is an electrolyte that is dissociated or protonated in aqueous solution under the experimental conditions used. These interactions, that can be either attractive or repulsive, strongly depend on the charge densities for both the carbon surface and the adsorbate molecule and on the ionic strength of the solution (Moreno-Castilla, 2004). Practically, the efficiency of activated carbon will mainly rely on its accessible surface area where physical adsorption takes place (pore size distribution), on the heteroatom content and the properties of the adsorbates. The influent micropollutant and DOC concentrations, contact time with the GAC, and type of GAC are major parameters influencing the adsorption. It is also interesting to note that adsorption from solution is essentially an exchange process, and hence molecules adsorb not only because they are attracted by solids but also because of their low affinity with the solvent (Moreno-Castilla, 2004) due to hydrophobic effect. Thus, the characteristics of the solution chemistry and the adsorption temperature are also parameters influencing the adsorption process and breakthrough of the micropollutant across GAC systems (Schreiber et al., 2005).

Activated carbons exhibit a high degree of porosity and an extensive internal surface area. Activated carbon is also used in the treatment of municipal and industrial wastewater due to its ability to adsorb a wide variety of pollutants. Adsorption processes do not add undesirable by-products to drinking water, but high adsorbent usage rates can be expected if activated carbon is employed to adsorb polar organic contaminants. The adsorption isotherms express the amount adsorbed per unit mass of adsorbent as a function of the equilibrium concentration in solution. However, this practice should be viewed with caution when determining the degree of exhaustion of a carbon in use, as chemical interactions with the already adsorbed compounds may affect the adsorbate uptake. Batch equilibrium tests are often complemented by dynamic column studies to determine system size requirements, contact time and carbon usage rates.

3.5 Factors Influencing Adsorption

3.5.1 Carbon Pore Texture

The micropore size distribution of adsorbents is an important factor, because the volume of pores in a size range similar to the molecular size of the targeted contaminant determines the adsorption capacity of a given adsorbent (Li et al., 2002, Rossner et al., 2009). Most of the adsorption on activated carbon takes place in the micropores as a consequence of the enhanced adsorption potential of the pore walls. However, the adsorption capacity of carbon materials is not related in a simple form with their surface area and porosity. The adsorption capacity will depend on the accessibility of the organic molecules to the inner surface of the adsorbent, which depends on their size. Thus, under appropriate experimental conditions, small molecules such as phenol can access micropores, natural organic matter (NOM) can access mesopores, and bacteria can have access to macropores. Because the diffusion through the micropores is usually the rate controlling step in the case of granular adsorbents (Moreno-Castilla, 2004), the suitability of a given activated carbon for a particular application depends on the ratios in which pores of different dimensions are present. A well-developed meso- and macroporosity is required to accelerate the kinetics of the adsorption process or for the adsorption of larger molecules such as found in some solutions.

3.5.2 Carbon Surface Chemistry

The surface chemistry of activated carbons depends mainly on their surface heteroatom content. The presence of oxygen and nitrogen in the form of functional groups has a major impact on the adsorptive properties of activated carbon, especially for polar or polarisable molecules. They determine the charge of the surface, its hydrophobicity, and the electronic density of the graphene layers. Thus, when a solid such as a carbon material is immersed in an aqueous solution, it develops a surface charge that comes from the dissociation of surface groups or the adsorption of ions from solution (Radovic et al., 2000). This surface charge will depend on the solution pH and the surface characteristics of the carbon.

Surface oxidation during the production of activated carbon by physical activation results in different types of oxygen surface groups. Oxygen surface groups are not formed exclusively by reaction with oxygen, but they can result also from reaction with many other oxidising gases (ozone, carbon dioxide, nitric oxide, etc.) and with oxidising solutions (nitric acid, sodium hypochlorite, hydrogen peroxide, etc.). The nature and amount of oxygen surface groups of a given activated carbon are affected by its surface area, particle size, ash content, and the conditions used for its manufacture. Oxygen groups are by far the most important in influencing the surface characteristics and adsorption behaviour of activated carbons (Rodríguez-Reinoso et al., 2001). Results obtained with activated carbons of different origins can be explained by the fact that oxygen complexes reduce the electronic density of the graphene layers and consequently reduce the basicity of the carbon surface (Moreno-Castilla, 2004). In addition, surface oxygen complexes also affect the surface hydrophobicity, which determines the hydrophobic effect.

3.5.3 Carbon Mineral Matter Content

Finally, the other characteristic of the adsorbent that controls the adsorption process is its mineral matter or ash content. This has, in general, a deleterious effect on the adsorption because it can block the porosity of the carbon matrix and can preferentially adsorb water due to its hydrophilic character, in this case reducing the adsorption of the adsorbate.

3.5.4 Adsorbate Properties

The observed diversity of removal efficiencies for various compounds by the same activated carbon is attributable to the diverse physicochemical properties of these compounds. Among the characteristics of the adsorbate that mainly influence the adsorption process are its molecular size, solubility, charge and the nature of the substituent(s) if they are aromatic. The molecular size controls the accessibility to the pores of the carbon and the solubility determines the hydrophobic interactions. The charge influences electrostatic interactions with the activated carbon surface. The charge of the adsorbate depends on the presence of acidic and basic functions, their respective pKa and the solution pH. Thus, the solution pH determines the carbon surface charge and the dissociation or protonation of the electrolyte. Ionic strength is the other key factor that controls the electrostatic interactions. Thus, these interactions, either attractive or repulsive, can be reduced by the so called “shielding effect” measurable by the ionic strength of the solution. This is due to the surface charge produced by the added salt. Therefore, when the electrostatic interaction between the surface and the adsorbate is repulsive, or the surface concentration is sufficiently high, an increase in ionic strength will increase the adsorption. Conversely, when the electrostatic interactions are attractive, or the surface concentration is sufficiently low, an increase of the ionic strength will diminish the adsorption. These effects have been shown to take place with many weak organic electrolytes and polyelectrolytes, for instance, in the case of bisphenol A and NOM (Moreno-Castilla, 2004, Newcombe and Drikas, 1997).

3.5.5 Temperature

Adsorption is generally accompanied by release of energy, that is, most adsorption processes are exothermic in nature. Adsorption being a spontaneous process, the effect of temperature on the adsorption is expected to increase the uptake of organic molecules when the adsorption temperature decreases. However, some examples have been reported where the amount adsorbed increased with temperature. For instance, it has been reported that the adsorption of paracetamol from diluted aqueous solution increased with temperature (Terzyk et al., 2003). This effect was independent of the type of carbon, its surface chemistry or solution pH. The authors attributed this behaviour to phase changes in the crystal form of the adsorbate.

3.5.6 Impact of EfOM on Adsorption

EfOM is present at concentrations 10^3–10^6 times higher than the micropollutants of interest. Based on this fact alone, decrease of micropollutant adsorption capacity is to be expected in the presence of EfOM (Pelekani and Snoeyink, 2000). Equilibrium and kinetic studies have shown that background organic matter (expressed in terms of DOC) can significantly reduce both adsorption capacity and kinetics for organic compounds on GAC (Yu et al., 2009, Ternes et al., 2002). Mutual competition effects between pharmaceuticals for the adsorption sites are expected to be negligible compared to competition with DOM.

It is commonly accepted that the background DOM first takes up the high energy sites and also blocks the pores through which the micropollutant molecules access adsorption sites. However it is still unclear which of the interaction mechanisms is dominant and how this changes when NOM has already adsorbed onto the carbon (de Ridder et al., 2011). With regards to the molecular size effect of DOM, Newcombe et al. (2002) explained that the low-molecular-weight fraction larger than 2-Methylisoborneol (MIB) molecules diffuses into mesopores and is subsequently adsorbed onto secondary micropores, thus totally blocking access to adsorption sites within the micropores. Meanwhile, the higher molecular weight DOM (10-30 g mol^{-1}) adsorbs only at or near the external carbon surface, not affecting the adsorption of MIB significantly (Newcombe et al., 2002). Similarly, Kilduff and Karanfil (2002) showed that GAC loaded with humic substances of molecular weight greater than 3,000 g mol^{-1} adsorbed similar trichloroethylene amounts to virgin GAC; while GAC preloaded with humic substances of molecular weight less than 3,000 g mol^{-1} adsorbed less TCE than the virgin GAC. As an explanation for the different effects of the two molecular weight classes of DOM, the authors suggested that lower molecular weight DOM could occupy the portion of the GAC that contained smaller pores, of diameter less than 1 nm, which the larger molecular weight fractions could not reach. A discrepancy between results from tests in pure water, natural water and wastewater was confirmed by several studies, highlighting that tests in pure water may overestimate the efficacy of activated carbon when used in natural water (Sabaliunas et al., 2003, Snyder et al., 2007a, Yu and Chu, 2009). Also, EfOM can have the effect of changing the surface properties of the carbon grains and is expected to lead to a shortened bed service life. Because the DOM is largely irreversibly adsorbed (Summers and Roberts, 1988) the permanent reduction in adsorption capacity is termed “carbon fouling”. A shift toward lower values of adsorption constant k, is equivalent to a lower sorption capacity, also observed with increasing preloading time, as depicted by (Zimmer et al., 1988).

The removals of 29 micropollutants with GAC using bench-scale, rapid, small scale column tests (RSSCT) and in two full-scale utilities, were examined by (Snyder et al., 2007b). The published data demonstrated that GAC was capable of removing nearly all compounds by more than 90%; however, its efficacy was greatly reduced by NOM (Snyder et al., 2007). In addition, the observation on two full-scale GAC adsorbers showed that the regeneration of the used GAC restored some capacity in removing the investigated compounds (Snyder et al., 2007). Isotherms for naproxen and carbamazepine using two different carbons (coal-based and coconut shell-based) preloaded for 1, 3, 5, 8, and 16 weeks were determined by Yu et al. (2009). As expected, k_f values dropped substantially within the first 5-8 weeks. After 16 weeks, the k_f values for naproxen were less than 0.5% of their virgin carbon values. For carbamazepine, k_f on F400 carbon after 16 weeks was only 1.2% of the virgin carbon value, whereas on CTIF carbon it was approximately 30%. The impact of preloading can be expected to be more severe for hydrophilic (Snyder et al., 2007b) or dissociated solutes (Yu et al., 2009) such as naproxen. The observation of a more rapid breakthrough of more hydrophilic contaminants on GAC confirms the general relationship between log K_{ow} and removal efficiencies. This study also suggested that the GAC with a wide pore size distribution had considerably greater NOM loading after a prolonged period, leading to lower capacities. It can therefore be inferred that a GAC with a large fraction of pores in the size range of the target micropollutants and a small fraction of larger pores would be preferred.

The following mechanisms were reasoned based on experiments using adsorbates of different molecular weight (Pelekani et al., 2000):

- In the primary micropore region, which is inaccessible to the majority of DOM molecules, the dominant mechanism resulting in reduction of micropollutant capacity is pore blockage.
- In the secondary micropore region, where a substantial amount of DOM can adsorb, the dominant mechanism is direct competition for adsorption sites.
- Increasing the volume of secondary micropores relative to the volume of primary micropores reduces the competitive effect.

Adsorption batch experiments were carried out in ultrapure, waste and surface water and fresh and DOM preloaded GAC was used (de Ridder et al., 2011). While reduction in surface area was similar for both preloaded GACs, up to 50% lower pharmaceutical removal was observed on wastewater preloaded GAC (de Ridder et al., 2011). This was attributed by the authors to higher hydrophobicity EfOM, indicating that DOM competition may influence pharmaceutical removal more than pore blocking. These mechanisms are pH dependent but, when a layer of DOM has been adsorbed on the carbon, the carbon becomes negatively charged due to OM coverage, with an increasingly negative charge at higher NOM loading (Newcombe, 1994). This may promote electrostatic repulsion and reduce adsorption of NOM and anionic micropollutants. At a GAC dose of 6.7 mgL^{-1}, negatively charged pharmaceuticals were removed in the range 0–58%, while removal of positively charged pharmaceuticals was between 32 and 98% (de Ridder et al., 2011).

Breakthrough curves studied by Corwin and Summer (2010), using dynamic columns, indicate that GAC adsorption capacity is dependent on GAC particle size when DOM is present. It was hypothesized that pore blockage is the mechanism responsible for the dependence on particle size (Corwin and Summers, 2010). When pore blockage occurs in the larger GAC particles there is relatively more surface area behind the blockage becoming unavailable, which explains the reduced adsorption capacity compared to small GAC particles. Blockage of a pore may not be total and previous research indicates adsorption kinetics are more impacted by pore blockage than adsorption capacity (Knappe et al., 1999, Li et al., 2003). The importance of the impact of pore blockage or competition on micropollutant removal is dependent on GAC properties, but also the micropollutant properties.

No direct competition between atrazine and background DOM was identified in the study by Knappe et al, 1999 on a GAC preloaded for five months, suggesting that the available sites on preloaded GAC were accessible to atrazine molecules but not to background DOM after the GAC was fully preloaded. Two possible mechanisms may contribute to this observation. If the adsorbate is small enough to access the primary micropores: (1) a fraction of the adsorption capacity for the target compound cannot be competed for by DOM, thus leading to a minimum value even after extensive preloading (Yu et al., 2009); and (2) a hydrophobic compound could partition to the “organic solution” formed at long preloading times (Yu et al., 2009).

However, the adsorptive capacity continuously reduced on GAC preloaded for 20 and 25 months, even after the GAC was totally exhausted at five months (Knappe et al., 1999). Two possible mechanisms may contribute to this observation. First, the weakly adsorbed DOM was replaced by more strongly adsorbed DOM (Roberts and Summers, 1982), therefore further reducing the adsorption sites for the target compound. Second, the adsorbed DOM became reoriented in the GAC particles, hence blocking more pores. The latter was hypothesised by Summers et al. (1989) in the explanation of the change of mass transfer rates on preloaded GAC.

3.5.7 Hydraulics

A reduction in the rate of organic compound adsorption is often observed with carbons preloaded with DOM. This may be due to an increased diffusion resistance at the particle surface, an intraparticle diffusion resistance, or both (Kilduff and Karanfil, 2002). Theoretically, the film diffusion should be constant when hydrodynamic conditions do not change in a certain GAC adsorber system. However, as preloading time increased, the film diffusion coefficient (β_L) decreased in some studies (Knappe et al., 1999, Carter and Weber, 1994). For TCE adsorption from river water, Carter and Weber (1994) showed that the β_L on virgin GAC was 2.5 times larger than that on GAC preloaded for three weeks. It was also found that the β_L determined for adsorbing atrazine on GAC preloaded for five months dramatically decreased compared to that on virgin GAC; however, longer preloading times only had a slight effect on β_L (Knappe et al., 1999). The exact reasons and mechanisms for decreasing β_L values due to preloading have not been clarified to date (Yu et al., 2009). However, Carter and Weber (1994) suggested two possible reasons. 1) The local viscosity of the film surrounding a GAC particle increased due to preloading, resulting in decreased diffusion rates of micropollutant molecules across the hydrodynamic boundary layer. 2) Some effective area for mass transfer flux into the carbon particle is blocked by preloaded background NOM, leading to reduced film diffusion flux.

3.6 Regeneration

Regeneration is the term used to describe some processes used to recover the adsorptive capacity of the spent carbon: chemical oxidation of the adsorbed material, steam to drive off the adsorbed material, solvents, and biological conversion (or bioregeneration). Activated carbon only transfers pollution from the liquid to a solid phase and does not decompose them into harmless substances. After usage, AC may be cleaned and reused, and the impurities discarded. Regeneration has the considerable potential of lowering costs for users over long term, but rising disposal costs for spent carbons are also increasing demand for reactivation. Therefore it is necessary to consider the methods for decomposition of adsorbed micropollutants. The simplest procedures for desorbing adsorbed substances are by heating or pressure reduction, but extraction with solvents is recommended in some cases to remove adsorbed substances from the spent carbon. A method for regenerating spent activated carbon has been introduced in which desorption is carried out with liquid water under subcritical conditions (Rodríguez-Reinoso et al., 2001). Nevertheless, the chemisorbed part cannot be desorbed, even at high temperatures, and it is converted to light gases and heavy products that evolve from the surface of the carbon, and also to a polymeric carbon residue that remains on the surface. This residue reduces the adsorption capacity of thermally regenerated activated carbons, and adsorption capacity often decreases when the number of regeneration cycle increases (Moreno-Castilla, 2004).

Factors that influence the adsorption process are the characteristics of the adsorbent and adsorbate, the solution chemistry and the adsorption temperature. Among them the chemistry of the carbon surface has a great influence on both electrostatic and non-electrostatic interactions, and can be considered one of the main factors in the adsorption mechanism from dilute aqueous solutions.

EfOM also affects adsorption by different mechanisms: 1) direct competition, in which small DOM molecules simultaneously compete with target compound molecules for access to the adsorption sites on activated carbon; and 2) pore blockage by DOM, in which large molecules accumulate and block the openings of small pores, preventing target compound molecules from accessing adsorption sites. Also, the presence of a surrounding viscous layer has an impact on the hydraulics around the carbon grains, creating a resistance to diffusion of molecules toward the surface and in the pores of the carbon grains. In general, the impact of preloading can be expected to be more severe for less adsorbable micropollutants (hydrophilic or dissociated solutes) and at high equilibrium concentrations.

4. BIOLOGICAL ACTIVATED CARBON (BAC) FILTRATION

4.1 General Principles

Over time, adsorption sites in GAC become saturated with organic compounds and the activated carbon loses its initial effectiveness, the biofilm supported on GAC develops and the filter bed becomes biologically active due to the presence of bacteria which inhabit the pores of the carbon granules. This biological action ensures that the carbon, which is now termed BAC, continues to remove DOC by metabolic processes. The level of DOC removal by BAC is significant but less than that achieved by adsorption onto new GAC; however the effective life of a BAC filter is often over 10 years whereas the life of a GAC filter relying on adsorption processes alone can be as short as 3 months. Evaluation of the different fractions of DOC can indicate effluent quality but also provides further insight into the BAC treatment. Zhang et al (2010) divided the DOC into four different fractions and studied their removal in different running stages of a BAC filter:

- Non biodegradable and adsorbable fraction (NB&ADOC)
- Biodegradable and adsorbable fraction (B&ADOC)
- Biodegradable and non adsorbable fraction (B&NADOC)
- Non biodegradable and non adsorbable fraction (NB&NADOC)

After continuous running for five months or 14,600 bed volumes filtered, the adsorbability of activated carbon dropped obviously, which can be proved by the drop in removal of NB&ADOC from 42.8% down to 2.8%, but the BAC filter still had desirable removal efficiency for B&ADOC (about 91.5%) (Zhang et al., 2010). Interestingly, the removal of B&NADOC in BAC filter has gone from 4.35% in initial stage up to 46.43%, the reason of which may be explained as follows: although activated carbon has no adsorbability for this type of material, some extrapolymeric substances, such as polysaccharides produced by bacteria attaching to the activated carbon grains could adsorb B&NADOC and then removed them by biodegradation (Zhang et al., 2010). On the other hand, there are lots of suspended bacteria among carbon grains in a BAC filter bed, which could directly capture B&NADOC by physically holding it up and biologically adsorbing it; then removing material by biodegradation.

A theoretical representation of staged DOC removal by BAC treatment is shown in Figure 5 (Simpson, 2008). Periods A, B and C are characterised by processes of physical adsorption, concurrent adsorption/biological degradation and biological degradation, respectively.

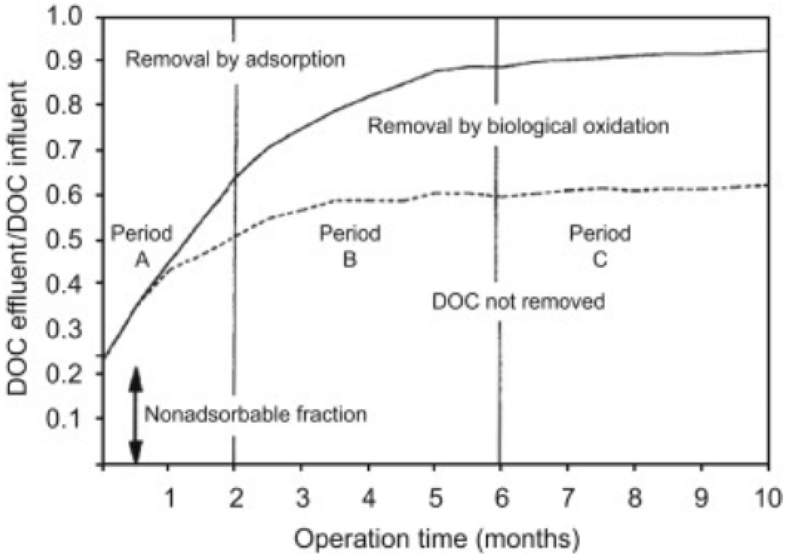

Figure 5: Theoretical representation of ozonated DOC removal by adsorption and biological degradation over time. (Note: the dashed and solid lines represent the amount of DOC removed from the influent by adsorption and biological degradation processes respectively). Reprinted from (Simpson, 2008) with permission of Elsevier.

The manner in which BAC filters and the associated biofilms remove or eliminate DOC from source water is thought to be a three-stage process. Initially, most of the DOC removal occurs through physical adsorption of the DOC to the GAC media where the bacteria in the associated biofilm are in an acclimation phase (Period A). This period lasts approximately 2–3 months (Simpson, 2008) or 3,000 bed volumes (Yapsakli and Çeçen, 2010). Of the total DOC removed from the source water, 10–20 per cent of the DOC is believed to be non-adsorbable on the GAC (Yapsakli and Çeçen, 2010, Dussert and Van Stone, 1994). In period B, DOC removal by adsorption gradually decreases as the GAC adsorption sites become saturated with DOC. The degree of biological degradation of DOC also increases significantly during this time. Thus, Period B exhibits parallel processes of DOC adsorption and biological degradation (Simpson, 2008). In Period C, the rate of DOC removal from source water reaches a relatively steady state. In this phase, biological oxidation is the predominant process responsible for DOC removal, since most of the adsorption capacity of the GAC is deemed exhausted (Dussert and Van Stone, 1994). Biodegradation in BAC filters removes part of the BDOC resulting in a decrease in the DOC concentration and in a reduction of DOC loading on the carbon. The reduced DOC loading results in less competition: more adsorption sites remain available for adsorption of micropollutants (van der Aa et al., 2006). At this stage in the water filtration process, DOC removal efficiencies range from 15 to 45 % (Simpson, 2008). If the removal efficiency obtained under steady state conditions meets the treatment objectives, the service life of GAC can be significantly increased.

From this point of view biodegradation in BAC should be maximised. The combination of ozonation and GAC was also found to significantly enhance the biological activity on BAC and can be referred to as the biologically enhanced activated carbon process. Ozonation by-products are generally very biodegradable and their removal within BAC filters leads to the control of biological regrowth in the distribution systems and an increase in stability of the residual chlorine. However, too much increase in biodegradability by pre-oxidation may result in incomplete removal of BDOC and biofilm formation in the distribution system. Also, excessive biomass production might contribute to unacceptably high backwash rates (van der Aa et al., 2006). The pores provide shelter to an amount of bacteria protected from the shear stress as can be seen on Figure 6.

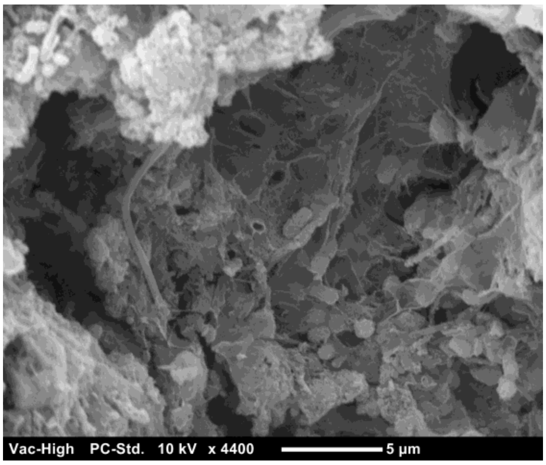

Figure 6: Scanning electron microscopy of the pore entry of a BAC particle exposed to 35,000 bed volumes of tertiary treated wastewater.

Activated carbon can further protect some bacteria against the negative influence of toxic substances (Scholz and Martin, 1997). The exportation of bacterial biomass into the effluent must be assessed when considering the BAC process. Servais et al. (1991) monitored the amount of bacteria in the outlet of the BAC filters used in a full scale drinking treatment plant in Paris before and after backwashing and observed that only 4 to 8% of the bacterial biomass attached to on GAC was released during the washing. The risk in a recycling scheme is present if human pathogens are exiting the BAC filters. This can be minimised by inactivation during post disinfection and an additional filtration step through sand to prevent escape of activated carbon fines in the product water.

4.2 Biofilm

Measurement of the adenosine tri-phosphate (ATP) content of GAC sampled from nine drinking water treatment plants treating either ground water or surface water; with or without oxidative pretreatment, showed that at least 6–125 g of dry weight (DW) of microbial biomass carbon is present in a filter bed containing 100 L of BAC (Magic-Knezev and van der Kooij, 2004, Magic-Knezev et al., 2009). In another study, the method was applied for the investigation of biofilm formation during the start-up period of a GAC pilot-scale plant treating Lake Zurich water (Velten et al., 2007). A rapid increase in the biomass of up to 1.1×10^{10} cells g_{GAC}^{-1} dry weight (DW) within the first 33 days was observed, followed by a slight decrease to an average steady-state concentration of 7.9×10^{9} cells g_{GAC}^{-1} GAC DW (Velten et al., 2007). Most bacteria produce extracellular polymeric substances that take part in forming microbial aggregates.

Bacteria grow in suspended cultures or in biofilms. The microbial biofilm includes bacterial cells enveloped by a matrix of large polymeric molecules. By definition, extracellular polymeric substances are located at or outside the cell surface. The structure of the biofilm plays a significant role in the passage of waterborne substances from the liquid bulk flow to the GAC (Simpson, 2008). The transport of waterborne substances towards the GAC surface through this laminar film is primarily accomplished by molecular diffusion. As such, a reduction in the size of waterborne substances (via pre-ozonation) will also permit more substrate to diffuse through the biofilm towards the GAC sites (which will subsequently increase GAC adsorption). Work carried out at pilot plant scale comparing BAC and sand biofilters showed that BAC has a good potential for the removal of DOC (35 to 60%), PPCPs (>90%) and toxicity (baseline-TEQ: 28 to 68%) even without pre-ozonation, whereas biofilms on a sand bed with comparable dimensioning showed limited improvement of effluent quality (Reungoat et al., 2011).

Also, the properties of the biofilm (structure and charge) plays an important role in the passage of substances from the liquid bulk flow to the carbon surface (Simpson, 2008). Preloaded carbons usually obtain a negative surface charge as a consequence of accumulation of DOM on their surfaces increasing interactions with positively charged compounds. However the diffusion coefficients of trace pollutants inside microbial biofilms are expected to be lowered by several orders of magnitude for most compounds and therefore the diffusion through the biofilm may be limiting the adsorption on the carbon surface. The kinetics of the exchange of hydrophobic organic compounds between aqueous phase and microbial biofilm is still expected to be rapid, especially compared to biodegradation kinetics. Although molecular diffusion is believed to be the primary mass transport process within the biofilm, complex convective transport of waterborne substances has also been reported. As the biofilm proliferates, the microbial cell clusters and exopolymeric substances form a relatively porous structure which is separated by interstitial voids and open channels (Simpson, 2008). Due to this porosity, some waterborne nutrients and micro-organisms can pass through the biofilm's water filled channels toward the GAC surface (Simpson, 2008).

4.3 Removal of Micropollutants in BAC Filters

Before exhaustion, adsorption and biodegradation are known to be the predominant mechanisms contributing to DOC removal in BAC columns. The difference between the influent and the effluent DOC concentrations after exhaustion can be attributed mostly to biodegradation (Yapsakli et al., 2010). For micropollutants, BAC probably combines the adsorption by GAC with the biosorption on the biofilm and possible degradation by the microorganisms for a longer extent as the adsorption sites for micropollutants are different from those for DOM. It potentially results in a more effective and resilient treatment system for aqueous solutions, with relevant concentrations of some specific organic compounds. Unfortunately, it is difficult to identify their relative importance at different operational stages. Under sterile conditions only, the removal by adsorption alone can be determined.

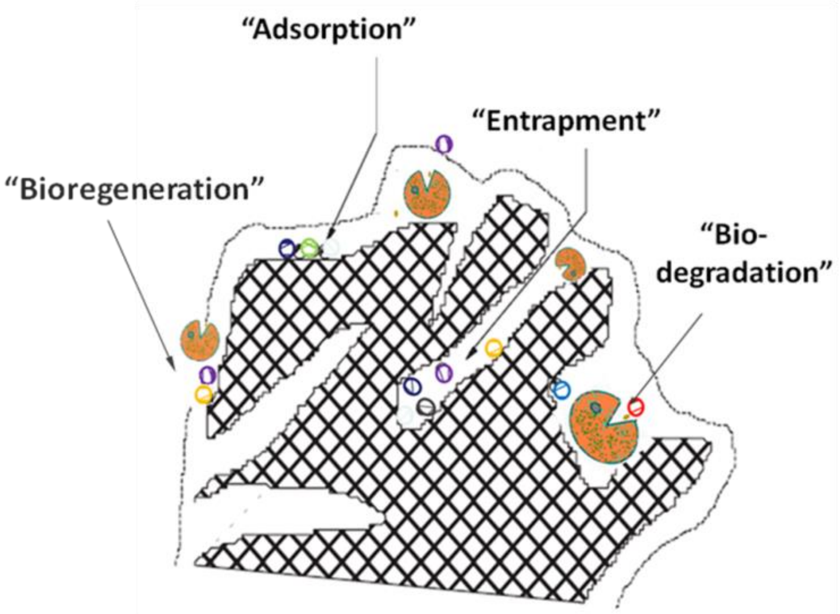

Figure 7: Biological Activated Carbon removal mechanisms. Adapted from Simpson (2008).

Biofilms growing in biologically active filters make up a diverse microbial community (Zhang et al., 2011). As represented in

Figure 7, the attached microbial biofilm is capable of breaking down and removing adsorbed substances in a process known as "biodegradation" participating in the treatment by removing BDOC, and may degrade MPs present in secondary treated wastewater. A similar effect has been observed for cyanotoxins in drinking water treated with biological activated carbon (BAC) (Wang et al., 2007). In addition to biological degradation and adsorption, there is still another BAC mechanism that contributes to contaminant removal from source water. BAC microbial biofilms are capable of bioregeneration, a mechanism known to renew activated carbon media by microbial activities (Aktas and Cecen, 2007). The effectiveness of BAC biodegradation/bioregeneration depends on numerous factors besides reversibility of adsorption and biodegradability of the adsorbates, such as the ability of the microbial population to biodegrade the substrates and potentially the micropollutants.

The principal theory regarding bioregeneration is the hypothesis of desorption by exoenzymatic reaction (Nath and Bhakhar, 2010). Indeed a biofilm containing bacteria in the macropores and their "exoenzymes" in the micropores can be established on BAC (Scholz and Martin, 1997). Adsorbed molecules are included in the biofilm and probably more exposed to enzymes produced; they may be responsible for compound elimination by co-metabolism. Being much smaller than a bacterial cell, these exoenzymes can diffuse into the mesopores and micropores of the activated carbon. Exoenzymes are believed to act on an adsorbed compound, inducing its hydrolytic transformation. The new products generated by this process may have a lower affinity for the activated carbon and therefore desorb, renewing adsorption capacity.

Snyder et al. investigated the removal of individual organic micropollutants in a full scale BAC filter (Table 2).

Table 2: Removal of EDCs and PPCPs with Full-scale BAC filter (ng L-1). Adapted from Snyder et al. (2006).

Compound	Raw Water (Secondary Effluent)	BAC Influent (ng L^{-1})	BAC Effluent (ng L^{-1})	BAC Removal (%)
Atenolol	763	719	14	98
Atrazine	5.2	4.1	7.8	<1
Bisphenol A	23	5.2	14	<1
Carbamazepine	272	232	48	79
Diazepam	1.6	1.3	0.4	69
Diclofenac	90	85	1.0	99
Dilantin	176	153	78	49
Fluoxetine	24	23	<0.5	>98
Gemfibrozil	24	18	3.5	81
Meprobamate	324	318	227	29
Naproxen	25	19	<0.5	>97
Norfluoxetine	1.6	1.4	<0.5	>64
Sulfamethoxazole	612	510	251	51
Triclosan	61	61	<1	>98
Trimethoprim	167	144	4.4	97

BAC was effective for some contaminants and ineffective for others. Again, it is difficult to discriminate the influence of both adsorption and biodegradation on the different compounds removals. Information about the time of service of the BAC used on the sampled plants are not available to assess which mechanisms (Period A, B or C in Figure 6) are responsible for the removal. Bacteria also tend to retain strongly many organic compounds, including dyes, phenolics and pesticides. According to Xiao et al. (2007), as the interior plasma membrane is impermeable to organic pollutants, the bacterial cell wall is expected to be the primary element responsible for organic biosorption. (Quintelas et al., 2010) studied the retention ability of a biofilm of *Arthrobacter viscosus* supported on GAC, for the removal of organic compounds from liquid solutions. The ability of *A. viscosus* to degrade phenolic compounds was assessed by parallel assays in which the biofilm was used in different forms, supported by GAC (attached form) but also without GAC to act as support and or as adsorbent (suspended form). Degradation occurred for phenol and for o-cresol but not for chlorophenol. Moreover, the degradation was detected just after a much longer period (13 days) than the one needed for biosorption/adsorption to reach equilibrium (5 days) (Quintelas et al., 2010). The use of bacteria supported on activated carbon allows combining of the good capabilities of both to retain and/or degrade organic compounds and, eventually, a synergistic effect is expected between support and biofilm. Indeed, BAC has been shown to have good potential for the removal of a wide range of micropollutants (>90%) and toxicity (baseline-TEQ: 28 to 68%) even without pre-ozonation, whereas biofilms on a sand bed with comparable dimensioning showed limited improvement of effluent quality (Reungoat et al., 2011). According to (Herzberg et al., 2003), an adsorbing biofilm carrier, like GAC, can be the source of an extra flux of pollutant to the biofilm thanks to the existence of some biofilm free areas. The same author compared a non-adsorbing granular carbon and a normal GAC, both loaded with an atrazine degrading biofilm and concluded that the higher biodegradation and lower atrazine concentrations in the normal BAC reactor were due to this double flux induced by a "patchy biofilm".

Biodegradation of organic compounds as a substrate is likely to happen when a compound undergoes desorption in the GAC column. The probable explanation is that microorganisms preferentially metabolise molecules that are freely suspended in the aqueous phase, rather than metabolising molecules that are already sorbed to the GAC. This choice can be motivated by the fact that molecules sorbed to the GAC offer greater resistance to biosorption than non-sorbed compounds because of the bonds existing between the molecule and GAC. Indeed, microorganisms preferentially utilise electron acceptors that provide the maximum free energy during respiration. The organics that have a greater affinity for activated carbon are less likely to be biodegraded and have a low adsorption-desorption rate because the compounds are less likely to be released in the aqueous phase (Shi et al., 2004). Therefore, the compounds most likely to be biodegraded are those that have the least affinity for GAC and therefore are the most likely to be found in the aqueous phase (Levine et al., 2000). On the other hand, adsorbed molecules are exposed to bacteria and their enzymes for a longer time than in non adsorbing filters. This potentially allows for biodegradation of slowly biodegradable compounds. The GAC can also attenuate spikes at high concentrations by first adsorbing the pollutants and then releasing them.

4.4 Parameters Affecting Performance of BAC

Actual bed contact time, or the length of time each volume of water remains in contact with the adsorbent, is an important variable to consider when using biologically activated carbon. Researchers have reported that 62 to 90 % of assimilable organic carbon was removed within 2 min. of contact time in BAC filters (Pipe-Martin et al., 2010). Rittmann et al. (2002) reported that empty bed contact time (EBCT) greater than 3.5 min had insignificant effects on DOC removal in pilot filters treating ozonated groundwater. An optimum EBCT for an ozone-BAC process treating raw waters was reported by (Li et al., 2006) to be 15 min. This does not mean that such optimal EBCTs are applicable for micropollutant removal, since their half lives are very variable and generally in the range of a day in activated sludge biomasses. However, diffusion through the biofilm together with the adsorption process on the GAC will increase the actual contact time between the micropollutant and the biomass, which will then be higher than the measured EBCT. This will in turn increase the likelihood of biodegradation by the biomass.

Decreasing the GAC particle size was found to be an influential factor. Indeed, Liang et al. (2007) modelled the mass transfer within the biofilm, another essential factor influencing the performance of BAC. Reynolds number, together with Sherwood and Damköhler numbers, were shown to increase as the particle size increases, and resulted in the mass transfer within the biofilm being the limiting factor of the performance of a BAC column (Liang et al., 2007). On the contrary, decreasing the particle size, the condition of lower Damköhler number, led to a lower biodegradation rate or a higher transfer rate within the biofilm. Therefore, more substrate diffuses across the biofilm, which increases the ratio of adsorption rather than biodegradation (Liang et al., 2007).

The hydraulic loading rate (HLR), and the backwashing regime are also parameters influencing the BAC process. Other important parameters are dissolved oxygen (DO), pH and a correct balance of nutrients, which enables a natural control of the biomass. Biological oxidation within GAC filters can also be efficient for the removal of inorganics such as ammonia (Dussert and Van Stone, 1994). It can be expected that the amount of essential nutrients present in the water will influence the growth of the biofilm and the type of bacteria on BAC.

The mix of organic compounds present can render the adsorption process more or less effective. Some studies have shown that BAC continues to effectively remove organics far beyond the point at which the adsorption capacity would normally be saturated. Biological processes offer a potentially useful alternative because frequent regeneration of the media is not required and biodegradable dissolved organic carbon (BDOC) is preferentially removed. Biodegradation and sorption are complementary mechanisms that extend the life of the GAC and delay organic breakthrough. Biofilms growing in biologically active filters are diverse microbial communities that may degrade micropollutants present in secondary treated wastewater. The potential synergistic effect on the fate of micropollutants between support and biofilm has to be investigated further. Noteworthy is another mechanism by which the biological activity potentially extends the life of BAC; so-called bioregeneration results in the maintenance of a significant adsorption capacity. Indeed, by using substances adsorbed on the carbon, the biomass can regenerate some adsorption sites readily available for other adsorbates.

5. OTHER BIOLOGICAL FILTRATION TREATMENT PROCESSES

5.1 Generalities

Secondary effluents can be upgraded by other biological treatments such as slow sand filtration (SSF), river bank filtration (RBF) or soil aquifer treatment (SAT). These geopurification or biofiltration techniques which represent wastewater reclamation/reuse technologies that can purify wastewater effluent to drinking water levels (Amy and Drewes, 2007) have the interesting potential to be a readily available, robust, effective and low energy intensity treatment technology. While biological removal of contaminants in drinking water is a process that has been utilised in the industry for many years, the full potential has not yet been reached. This is due to the lack of understanding of the many microbiological processes taking place within the biofilm. In addition, the inclusion of a groundwater recharge and recovery cycle may provide quality improvement of the effluent, as well as economic, aesthetic, and psychological benefits (no undesirable “toilet to tap” connection) as a result of the transition between reclaimed water and groundwater (Bouwer, 2002, Tchobanoglous et al., 2003). They therefore present an interesting alternative technology for indirect water reuse. It is important to determine the behaviour of constituents in treated sewage during further treatments by soils.

5.2 DOC Removal

Water treatment utilising biological degradation usually takes place on a fixed biofilm on a filter medium; for example, the “schmudzdecke” on slow sand filters. There are many advantages to this type of treatment as biological filter processes require relatively little maintenance and no addition of chemicals, relatively low infrastructure and running costs and achieve a significant removal of the fraction of the organic compounds in the water. Biological filtration processes have been recommended as a good tool to reduce biodegradable and assimilable fractions of DOC (Charnock and Kjønnø, 2000, Van Der Kooij, 2003) in the water entering reservoirs or distribution systems decreasing significantly the rate and extent of microbial growth and biofilm. Furthermore, biological aggregates, such as flocs and biofilms, have been found to be very efficient in removing even slow-degrading or non-degradable compounds, including colloidal and particulate matter (Pipe-Martin et al., 2010). The minimisation of organic compounds in water will also reduce the negative effects resulting from the use of chlorine in disinfection. Available data from municipal wastewater treatment systems suggest that many of the compounds are biologically transformable by bacteria so biological filtration processes may also provide a cost-effective option for further removal of EDCs and PPCPs from water (Snyder et al., 2003a).

5.3 Micropollutant Removal

The biological sand filter is a potentially efficient additional barrier for the elimination of any biodegradable contaminants. Indeed, measurements of the elimination of organic micropollutants in a municipal WWTP (Hollender et al., 2009) showed that the biological sand filter further eliminated a few compounds: diclofenac 20%, atenolol 15%, sotalol 15%, naproxen 30%, carbendazim 15%, and trimethoprim 15%. After an upgrade with ozonation prior to the biological sand filter, biodegradable compounds formed during ozonation (such as NDMA) were removed at a level of 50±17% (Hollender et al., 2009). Work carried out at pilot plant sand biofilters showed a DOC removal of about 22%. Among the 21 compounds selected, 12 were not or poorly removed ($\leq$ 20%), 8 experienced intermediate removal (23-54%) and only one compound, paracetamol, was well removed (85%) by the sand (Reungoat et al., 2011).

Retention times in soil are typically between 6 and 12 months, depending on the pre-treatment, but most of the microbial assimilation occurs when the nutrient-loaded source water is introduced to the subsurface. Mechanisms, such as hydrogen bonding, would be related to the removal of more polar organic micropollutants. As mentioned previously, several studies have suggested that only compounds in solution, or readily desorbable, are available for degradation. However, experiments with atrazine suggested that bacteria can access specific regions where the herbicide is sorbed and that the concentrations found support higher mineralisation rates than predicted on the basis of aqueous-phase concentrations (Park et al., 2004). Characteristics of high sorbed-phase concentration, chemotaxis, and attachment of cells to soil particles seemed to contribute to the bioavailability of soil-sorbed atrazine (Park et al., 2004). Data from sites where wastewater effluent is used to recharge aquifers indicate that many of the PPCPs are removed during the first few weeks of passage through the aquifer (Drewes et al., 2001b). However, certain recalcitrant compounds, including the antiepileptics, carbamazepine and primidone, and iodinated X-ray contrast media, persist during infiltration through vadose and saturated soil zones (Drewes et al., 2001b). Similar results were observed in bank filtration (Heberer, 2002) and during slow sand filtration in drinking water treatment plants.

Also, the formation of degradation compounds cannot be excluded, further research being essential to differentiate between sorption and degradation through the identification of degradation products (Ternes et al., 2007). Despite this, it is unquestionable that both aerobic and anoxic underground passage of recharge water can significantly lower the concentration of several organic microcontaminants present in the source water; however, the extent of reduction is often difficult to predict since several factors influence it (Díaz-Cruz and Barceló, 2008a). Degradation rates are known to vary with redox state, however, the half-life data of a wide range of organic chemicals are mainly defined by the presence or absence of oxygen, rather than the range of redox states (AGWR, 2009). Low dissolved oxygen/low nutrient conditions favouring long term persistence of organics (Díaz-Cruz and Barceló, 2008b). Aerobic processes appear to be responsible for the high degree of elimination of trihalomethanes and phenoxy pesticides, associated with the unavoidable formation of the hazardous chlorophenols due to the degradation of such pesticides (Díaz-Cruz and Barceló, 2008a).

5.4 Removal Mechanisms and Influencing Parameters

In a study of 6 hydrophilic (logD<3) organic compounds of small molecular weight (below 360 g mol^{-1}) during their passage through a lab column simulating RBF in abiotic conditions, none of the 6 spiked organic contaminants (175-226µg L^{-1}) was attenuated (Rauch-Williams et al., 2010). A study of the sorption of carbamazepine and naproxen demonstrated that the sorption abilities of the DOM fractions can significantly affect the mobility of pharmaceutical compounds in soils influenced by intensive irrigation with treated wastewater (Maoz and Chefetz, 2009). Previous studies demonstrated that the type and bioavailability of EfOM controls the extent of soil biomass growth in MAR (managed aquifer recharge) systems (Rauch and Drewes, 2004, 2005). The concentration and character of bulk organic carbon present can vary (from less than 1 to up to 15 mg L^{-1} or more for the BDOC concentrations) depending the effluent fed to MAR systems and, as a consequence, the total biomass and diversity of soil microbial communities too. Due to the low ambient concentrations of trace organic contaminants (occurring in the ng L^{-1} range) it is unlikely that energy from micropollutant metabolism is enough for biomass maintenance and growth. Micropollutants could be transformed by co-metabolism (co-utilisation). EfOM may consequently affect the degradation of trace organic contaminants by serving as a primary substrate in microbiologically facilitated transformations (Stratton et al., 1983). Acclimation of microorganisms to an organic carbon source plays a vital role and the biodegradation rate of many compounds increases after an initial lag time (Musson et al., 2009). Lim et al. (2008) observed that contaminants such as sulfamethoxazole were less difficult to remove in BDOC derived from aquatic plants, compared to BDOC derived from wastewater effluent dominated surface water. The variation in biotransformation rates of test compounds in biofilms receiving different sources of BDOC was attributed to the differences in microbial diversity and functionality among the microcosms. A recent study (Rauch-Williams et al., 2010) confirmed that the concentration and character of bulk organic carbon present in effluent affect the degradation efficiency for trace organic micropollutants during recharge operation. Specifically, aerobic, oligotrophic microbiological soil environments present favourable conditions for the transformation of trace organic chemicals, including rather recalcitrant compounds such as chlorinated flame retardants (Rauch-Williams et al., 2010). It was also observed by the same author (Rauch-Williams et al., 2010) that, in biotic conditions, during the 2nd and 3rd spiking event, 4 out of 6 micropollutants (ketoprofen, phenacetine, gemfibrozil, and naproxen) exhibited increasingly better removal, exceeding 95% 22 days after the first spike. The author concluded that the microbial community had adapted to metabolising the micropollutants. Nevertheless a modification of the microbial population itself due to exposure to the active compounds may be not out of the question.

Anaerobic microbial mineralisation of recalcitrant organic pollutants is also a significant component of the natural attenuation in the environment. In particular, hydrocarbons and halogenated compounds have long been doubted to be degradable in the absence of oxygen, but the isolation of unknown anaerobic hydrocarbon-degrading and reductively dehalogenating bacteria during the last decades provided ultimate proof for these processes in nature (Heider and Rabus, 2008). Recently, it has become apparent that some organisms, including *Desulfitobacterium chlororespirans*, can use certain brominated compounds, such as the herbicide bromoxynil and its major metabolite, as electron acceptors for growth. Iodinated compounds may be dehalogenated as well, though the process may not satisfy the need for an electron acceptor (Cupples et al., 2005).

Pesticide degradation by anaerobic processes, especially for chlorinated pesticides, has been proved to be more effective than that of aerobic processes (Ghosh and Philip, 2006). Stucki et al. (1995) has observed rapid biotransformation and mineralisation of atrazine by enriched microbial culture under denitrifying condition. With an initial atrazine concentration of 7.5 mg L^{-1}, within 30 minutes, the effluent atrazine concentration was 10-100 µg L^{-1}. Hydroxyatrazine was the main primary metabolite with a concentration range of 250-780 µg L^{-1}. Bacterial isolate *M91-3* (Crawford et al., 1998) was able to utilise atrazine as its sole source of carbon and nitrogen under anoxic conditions. The metabolite detected was hydroxyatrazine.

In another study it was observed that Cyanazine, another pesticide, competitively inhibited *M91-3* bacterial isolate in atrazine degradation (Gebendinger and Radosevich, 1999). *Pseudomonas sp.* Strain *ADP*, a gamma proteobacterium found in aquifer sediments and BAC filters, could mineralise 55% and 75% of atrazine in 2 and 4 days respectively under denitrifying conditions (Shapir et al., 1998).

It was observed at a bank filtration site, where transition from anoxic to anaerobic conditions takes place during the infiltration process, that the concentration of sulfamethoxazole can be reduced to 20% of the surface water concentration (Grünheid et al., 2005). In comparison, infiltration basins operating under aerobic conditions appeared to be less efficient, since the concentration is reduced only to 50% (Grünheid et al., 2005). During the biotransformation step, some studies have shown that anaerobic biological processes can be used for dechlorination. Biodegradation can transform organic chlorinated compounds to daughter compounds and subsequently to CO2 and CH4 under anaerobic conditions. The microbial biotransformation of tetrachloroethylene perchloroethylene (PCE) to trichloroethylene (TCE) and cis-1,2-dichloroethylene (cis-1,2-DCE) under anaerobic conditions was shown in a BAC filter (Wu et al., 2000).

5.5 Evidencing Biodegradation of Micropollutants

Evidence for biotransformation can be provided by a qualitative or even quantitative measurement of biotransformation products. However, technical issues often arise when trying to measure transformation compounds at environmentally relevant concentrations. Their instability and small amounts mean low concentrations of these compounds. Quantitative measurement by enantioselective analysis has also been used previously. Whereas in the abiotic processes the fate of enantiomers is generally not affected by the stereochemistry, biological processes may discriminate between enantiomers of chiral compounds and result in the enrichment of one of the enantiomers compared with the other (Pérez and Barceló, 2008). In fact, as a result of its interaction with enzymes or other naturally occurring chiral molecules, one enantiomer might be less persistent in the environment than the other. Stereoisomer quantification of the propranolol in wastewater has been carried out (Fono and Sedlak, 2005, Lai et al., 1993, Nikolai et al., 2006). The enantiomeric fraction (the ratio of the concentration of one of its isomers to the total concentration) of propranolol in the influent of five wastewater treatment plants was 0.50±0.02, while after secondary treatment it was 0.42 or less (Fono and Sedlak, 2005). Although metoprolol, which is administered as a racemate, is partially metabolized prior to excretion and is removed to a small extent in municipal wastewater treatment plants, it does not appear to undergo a net enantiomer shift during these processes (i.e., an average EF of 0.50±0.03, n=18) was observed for metoprolol by Fono et al. (2006) in the effluent of Dallas-area WWTPs. The same authors measured the average EF in the receiving river decreasing with distance downstream from 0.44 to 0.31 more than 200 km further. Measurements of enantiomers of other β-blocker drugs such as atenolol and metoprolol were also showing varying enantiomeric fractions between influent and effluents of two wastewater treatment plants (Nikolai et al., 2006). In another study, a pure bacterial culture, Sphingomonas herbicidovorans sp. nov. was able to degrade both enantiomers of mecoprop to completion (Zipper et al., 1996). However, the (S) enantiomer disappeared much faster from the culture medium than the (R) enantiomer (Zipper et al., 1996).

Engineered biofiltration techniques are popular as they achieve a significant removal of the degradable fraction of the organic compounds in water at low infrastructure and operational cost. Aerobic processes appear to be responsible for the high degree of elimination of most of the biodegradable compounds. The concentration and character of bulk organic carbon present in the water matrix can influence the removal of trace organic contaminants. Also, in recent years, substantial progress has been made in the understanding of anaerobic degradation of particular compounds and chlorinated pesticides were shown to be better degraded under anaerobic conditions.

6. CONCLUSIONS

The occurrence of a growing number of micropollutants has complicated wastewater treatment, since several compounds have been found to be resistant to biodegradation (Snyder et al., 2004). Indirect potable water reuse through biological filtration raises concerns (introduction of EfOM and persistent organic pollutants in the drinking water). To eliminate these doubts, and attenuate their impacts on the environment, treatment processes have to remove biodegradable fractions of the DOC and trace organic pollutants efficiently. Some sites cope with this task very well using biological filtration (SSF, RBF, SAT or BAC). However the physical, chemical and biological removal processes induced for the different contaminants are not sufficiently understood. Efforts should thus be focused on determining the reasons behind the success of biological systems and optimising the processes as cost effective treatment options that do not generate additional side streams requiring further treatment and disposal. From that point of view, mechanisms behind BAC performance need further investigation to elucidate the roles of biodegradation and adsorption in the removal process. This will allow for determination of the significance of BAC filtration for wastewater treatment within future process schemes.

The actual biodegradability of any organic compound, while dependent on the chemical structure of the molecule, is also highly dependent on other factors. WWTPs showed the impact of extended HRT on micropollutant removal and SAT, by its conception, provides extended contact time, resulting in further micropollutants being eliminated. One of the reasons for the performance of BAC is the increased contact time between the biofilm and the adsorbed compounds. Acclimation of microorganisms to an organic carbon source plays a vital role and the biodegradation rate of many compounds increases after an initial lag time. The presence of an appropriate microbial community, sufficient acclimation time, pH, temperature, presence of oxygen, redox potential; all are believed to influence the degradation of a compound. Desorbability is also suspected to have an influence on the biodegradation processes. The adsorbability of a compound on activated carbon is also influenced by several factors such as the characteristics of the adsorbent (pore texture, surface chemistry) and adsorbate (molecule size, hydrophilicity, charge), the solution chemistry, the temperature, the presence of organic matter (competition and pore blockage) and biofilm.

BAC is a composite particle of activated carbon with biotic components and, as such, micropollutant removal by such filters can be by either adsorption or biodegradation or both. Both biodegradation and adsorption are known to be evolving components of BAC treatment, during which parent compounds are removed from the aqueous phase. However, it is difficult to separate the influence of biodegradation or adsorption from the overall performance of BAC. Processes involving multi-component mixtures and competitive adsorption present complexity with regard to evaluating adsorption and biodegradation. Research to further understand the removal mechanisms in the BAC filters should focus on elucidating:

1. The participation of adsorption in micropollutant removal by BAC filters:

Most of the targeted compounds are known to be effectively removed by adsorption on GAC until EfOM preloading decreases the rate of micropollutant adsorption. However, the separated participation of adsorption in the removal of PPCPs and EDCs by BAC has not been evaluated yet. The adsorption capacity by BAC can be evaluated after inhibiting the biomass on the BAC media. A significant removal by adsorption on BAC can be expected, even after the exhaustion of the DOC removal due to EfOM preloading. More information on the decrease of the adsorption of micropollutants for a wide range of compounds characteristics is needed in order to better characterise micropollutant removal mechanisms during the BAC lifetime.

2. The participation of biodegradation in micropollutant removal by BAC filters:

Periods characterised by processes of physical adsorption, concurrent adsorption/biological degradation and biological degradation are expected for biodegradable organic micropollutants. The concentration and type of EfOM may influence the biodegradation of micropollutants, but also the bioregenerabilty of activated carbon, as OM molecules can compete for adsorbent sites and promote desorption of micropollutants. Adsorption desorption mechanisms can also play a role in the biodegradation of compounds. Different mechanisms are postulated to participate in the performance and extend the service life of BAC filters. However, there is no evidence of removal of mixtures of PPCPs and EDCs in BACs by biological processes. The participation of the biodegradation should be evaluated with different approaches, among which a long term comparison of the performance achieved by a BAC column to a GAC kept sterile.

3. Influence of the adsorption capacity on the biodegradation removal:

BAC should not be seen only as adsorptive media supporting a biofilm with two parallel micropollutant removal mechanisms occurring in parallel (i.e. adsorption and biodegradation). Following the mechanisms of bioregeneration, it is probably a medium of temporary storage for the contaminants through adsorption, which can be recovered through biodegradation. For this purpose, research needs to be completed to verify a potential advantage of BAC in term of biodegradation due to the phenomena: adsorption-bioregeneration. Media made of similar materials with different sorption capacities covered by similar microbial biomass can be used for this purpose. Micropollutants with detectable transformation by-products or/and measurable enantiomer ratio can be used in order to assess the extent of biodegradation.

4. The role of nitrifying bacteria in the micropollutant biodegradation:

The effectiveness of BAC biodegradation/bioregeneration depends on numerous factors, such as the ability of the microbial population to biodegrade the substrates and potentially the micropollutants. Ammonia-oxidising microorganisms associated with GAC have been observed previously. Biodegradation potential of several wastewater micropollutants by ammonia-oxidising bacteria has been shown previously in different systems, but the role of nitrifiers in the micropollutant degradation in BAC filtration has not been reported yet. To that end, the performance of the BAC should be evaluated after inhibiting the nitrifying activity on the BAC.

5. The potential of an anaerobic filtration step for the enhancement of micropollutant removal:

Despite the evidence that higher oxidation potentials in aerobic environments should favour their biodegradation, researchers have examined the anaerobic degradation of a number of organic micropollutants within WWTPs, MBRs and groundwater replenishment. The more diverse bacterial compositions within aerobic and anaerobic system may result in a greater removal for some compounds or/and a greater degree of degradation. For example, a compound may be partially biodegraded during aerobic treatment, with the resulting product then degraded fully in the denitrified system, thus optimising the BAC process. Moreover, removal mechanisms of micropollutants under different redox conditions are not yet understood in detail. Different degradation pathways in anaerobic and aerobic processes can be indicated by different transformation products. Understanding the behaviour of micropollutants under different redox conditions is not only essential for achieving deeper knowledge of wastewater treatment processes, but also in order to predict further pathways of those contaminants once released into the environment.

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