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Activated carbon coupled with advanced biological wastewater treatment: a review of the enhancement in micropollutant removal

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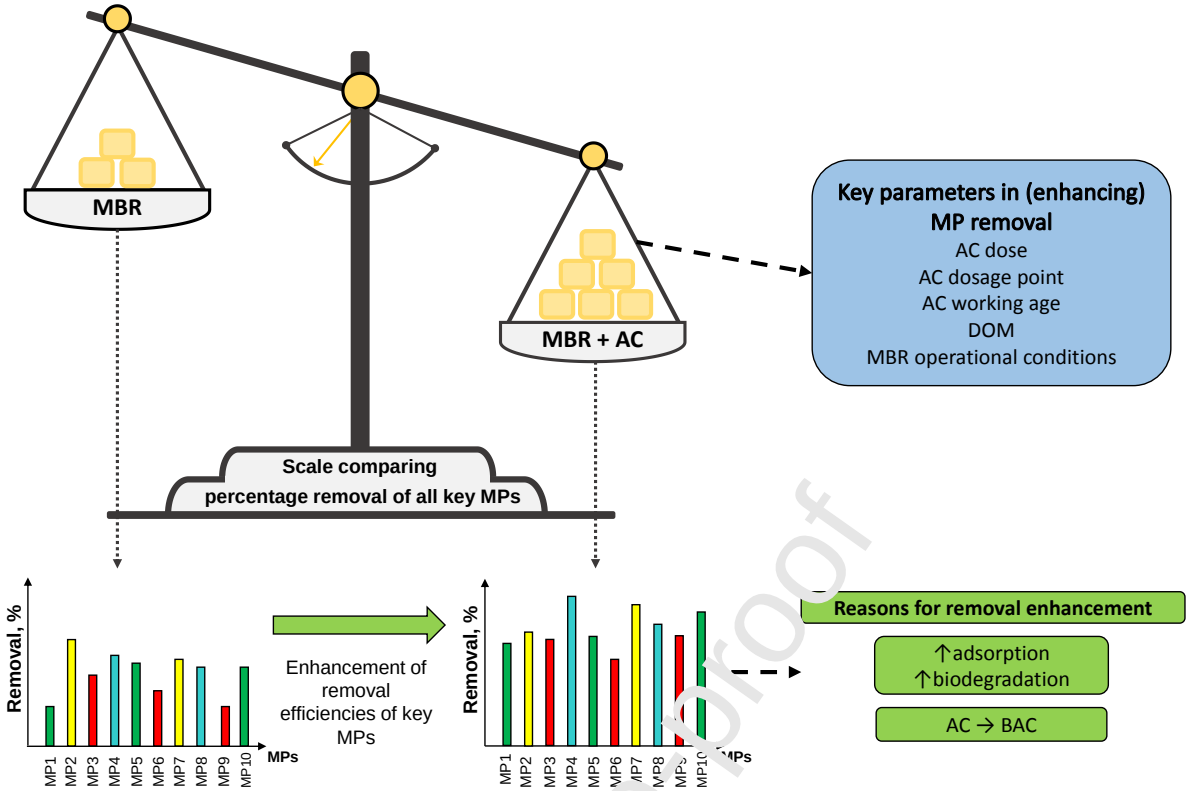
Abstract

This study consists of a review on the removal efficiencies of a wide spectrum of micropollutants (MPs) in biological treatment (mainly membrane bioreactor) coupled with activated carbon (AC), (AC added in the bioreactor or followed by an AC unit, acting as a post treatment). It focuses on how the presence of AC may promote the removal of MPs and the effects of dissolved organic matter (DOM) in wastewater. Removal data collected of MPs are analysed versus AC dose if powdered AC is added in the bioreactor, and as a function of the empty bed contact time in the case of a granular activated carbon (GAC) column acting as a post treatment ~~PT~~. Moreover, the enhancement in macropollutant (organic matter, nitrogen and phosphorus compounds) removal is analysed as well as the AC mitigation effect towards membrane fouling and, finally, how sludge properties may change in the presence of AC. To sum up, it was found that AC improves the removal of most MPs, favouring their sorption on the AC surface, promoted by the presence of different functional groups and then enhancing their degradation processes. DOM is a strong competitor in sorption on the AC surface, but it may promote the transformation of GAC in a biologically activated carbon thus enhancing all the degradation processes. Finally, AC in the bioreactor increases sludge floc strength and improves its settling characteristics and sorption potential.

Graphical abstract



Keywords Activated carbon, biological activated carbon, hybrid membrane bioreactor, micropollutants, removal efficiency, removal mechanisms.

Acronyms and Abbreviations

AC: Activated carbon
BAC: Biologically activated carbon
BET: Brunauer–Emmett–Teller
BOD_5: Biological oxygen demand
CAS: Conventional activated sludge
CEC: Contaminant of emerging concern
COD: Chemical oxygen demand
D617: 3-(3,4-Dimethoxyphenyl)-2-methyl-6-methylaminohexane-3-carbonitrile
DEET: N,N-diethyl-m-toluamide
DOC: Dissolved organic carbon
DOM: Dissolved organic matter
D_{ow}: octanol water partition coefficient
EBCT: empty bed contact time
E1: Estrone
E2β: Estradiol
E3: Estriol
EBV: Empty bed volumes
EE2: 17α-ethinylestradiol
EPS: Extracellular polymeric substances
GAC: Granular activated carbon
HRT: Hydraulic retention time
k_{biol}: Biological degradation rate
K_d: Solid liquid partition coefficient
K_{ow}: Octanol water distribution coefficient
LC-OCD: liquid chromatography organic carbon detection

LOD: Limit of detection
LOQ: Limit of quantification
MBR: Membrane bioreactor
MF: Microfiltration
MLSS: Mixed liquor suspended solids
MLVSS: Mixed liquor volatile suspended solids
MP: micropollutant
PAC: Powdered activated carbon
PFOA: Perfluorooctanoate
PFOS: Perfluorooctane sulfonate
pH_{PZC}: pH value at the point of zero charge
pK_a: Acid dissociation constant at logarithmic scale
PT: Post-treatment
RSST: Rapid Small Scale Column Test
SMP: Soluble microbial products
SRT: Sludge retention time
TMP: Trans-membrane pressure
TOC: Total organic carbon
UF: Ultrafiltration
WWTP: Wastewater treatment plant

1 Introduction

In the last two decades, there have been extraordinary developments in membrane technologies applied to wastewater treatment. Membrane bioreactors (MBRs) have become a widely used technology treating urban (Xiao et al., 2019) and industrial wastewater (Cattaneo et al., 2008). The combination of a biological treatment with a membrane separation provides a better-quality effluent over conventional activated sludge systems (CAS) regarding many regulated contaminants, in particular suspended solids and microorganisms.

Among the improved characteristics, MBRs have a lower footprint than CAS, can operate with a wide-ranging loading influent due to a higher biomass concentration and produce less excess sludge (Sipma et al., 2010).

One of the main drawbacks of MBRs is membrane fouling which leads to an increment in the operational and maintenance costs and a reduction in the membrane effective lifespan. However, accurate membrane maintenance planning can counteract it (Xiao et al., 2019).

Depending on the nature of the influent and the required effluent quality, promising insights have been obtained in recent years using advanced biological systems (MBRs) in combination with innovative treatment technologies: these systems are often called hybrid MBRs (Alvarino et al., 2017) or integrated MBRs (Neoh et al., 2016; Woo et al., 2016). Some have been consolidated, such as activated carbon (AC) and ozonation, while others have not yet been intensively implemented, such as advanced oxidation processes, membrane distillation bioreactors, biofilm/bio-entrapped MBRs, and nanofiltration/reverse osmosis

(Rizzo et al., 2019). In fact, hybrid MBR is designed not only to guarantee specific effluent quality, but also to improve the MBR operation. In this way, the use of adsorbents, such as AC, to mitigate membrane fouling has been the subject of research efforts in recent years (Iorhemen et al., 2017).

Wastewater treatment plant (WWTP) influent is characterised by a high content of organic matter. Of all the substances commonly found, there has been a focus on micropollutants (MPs) in recent years (Verlicchi et al., 2012). MPs consist of substances from natural and anthropogenic sources and, although their origin can be very diverse, they are strictly correlated to mass-produced materials for anthropogenic activities. While most MPs in WWTP influents range from ng/L to µg/L, some can exhibit higher concentrations (Verlicchi et al., 2012). In this context, biological treatments (mainly CAS and MBR) have not been designed to remove MPs from wastewater, but conventional macropollutants (namely suspended solids, organic substances, nitrogen and phosphorus compounds, microorganisms), and thus some of the most commonly consumed or recalcitrant MPs can be found in WWTP effluents at > 1 µg/L (Verlicchi et al., 2012).

Their vast occurrence and diversity, together with the lack of European regulations on their removal in WWTPs and their occurrence in the aquatic ecosystems (Rizzo et al., 2019), entail potential risks for human health and aquatic life, making them *contaminants of emerging concern* (CECs) in the sense clearly stated by (Barceló, 2003) and remarked more recently by (Sauvé and Desrosiers, 2014) and UNESCO (https://en.unesco.org/emergingpollutantsinwaterandwastewater). Their main characteristic is such that they may be subject to future regulations depending on monitoring data on their occurrence in the different aquatic environments, the results of research on their potential health effects and their contribution to the development of antibiotic resistant bacteria. Their persistence in the environment does not necessarily lead to negative effects, as their transformation or removal rates can be compensated by their continuous release into the environment. In the following, the term “micropollutants” will be used.

The high adsorption capacity of AC has been proposed as one of the most promising mechanisms to remove MPs from wastewater. Adsorption processes do not generate toxic by-products in comparison with other advanced technologies used in hybrid MBRs (*e.g.* ozonation, photocatalysis) and may also remove biological treatment inhibitors at the same time. One drawback to consider is the potential reduction in AC adsorption capacity due to the presence of dissolved organic matter (DOM) which is present in the stream under treatment (Guillossou et al., 2020; Margot et al., 2013). However, adsorbed DOM may

contribute to the development of microorganisms on the AC surface, enhancing biodegradation processes by the attached biomass (Fundneider et al., 2021b). In this way, design parameters and operational conditions that could contribute to increase the efficiency of the hybrid systems are crucial (Grandclément et al., 2017).

The inefficacy of conventional treatments in removing MPs determines the need for combined systems able to promote different removal mechanisms which could assure a reduction in MP levels and a lower impact on the receiving waters (Rizzo et al., 2019; Siegrist and Joss, 2012). The enhancement of MP removal by adsorption and biodegradation has therefore been studied among different configurations of MBR integrated with AC, both in the case of powdered activated carbon (PAC) or granular activated carbon (GAC).

This review aims to give a snapshot of the removal achieved for a wide spectrum of MPs from wastewater by means of hybrid MBRs, corresponding to MBRs where AC is added in the bioreactor and also to MBRs coupled with AC (in which the AC stage represents a polishing treatment) as well as of the quality (occurrence of MPs) in the final effluent of hybrid MBRs. The review attempts to respond to the following questions: Is it possible to increase the removal efficiency of selected MPs from wastewater by the addition of AC in an MBR or by coupling the MBR with a polishing AC treatment? What are the best PAC dosages or GAC bed characteristics to achieve the best MP removal efficiency? How does AC influence the MBR operation?

In order to provide the tools needed to answer these questions, an in-depth focus is first carried out on the main MP removal pathways occurring once AC is present in the wastewater under treatment and then a literature survey is presented and discussed on the removal efficiencies of a wide spectrum of MPs referring to different combinations of AC and MBR as well as applied operational conditions. The influence on MP removal of the main MP characteristics, AC properties, design and operational parameters and DOM presence is discussed as well as how AC may influence MBR operations, on the basis of lessons learned from collected studies.

2 Framework of the study

The review refers to a collection of peer reviewed papers identified by applying PRISMA guidelines (Moher et al., 2009). It first reports in detail how this collection was found, and then it discusses quality assurance criteria in order to include or exclude records (studies) and the data reported in them from the selected literature (see the section 3.1).

Briefly, the overview refers to the removal of MPs from wastewater by different configurations involving advanced biological treatments (namely MBRs) coupled with

activated carbon (Table 1). A spectrum of 179 MPs (Table 2), including 20 metabolites, belonging to 30 different classes, was considered: 142 pharmaceuticals, 8 personal care products (antiseptics, synthetic musks and UV filters) and 29 different industrial products (including non-ionic surfactants, stimulants, sweeteners, pesticides and compounds included in the group "Others"). Table S1 reports their main chemical characteristics (molecular weight, Log K_{ow}, Log D_{ow}, pK_a and charge).

A presentation is then reported of the main configurations of hybrid MBRs operating in combination with AC as well as in "ancillary" configurations where conventional activated sludge (CAS) treatments are combined with a post-treatment (PT), including a PAC contact tank followed by a UF membrane unit or a GAC column (section 3.2.1). The study continues by focussing on the interactions between AC and organic matter (MPs and DOM) as well as microorganisms when AC is added in the wastewater in the bioreactor or in the PT unit (Section 4). A first comparison is carried out between the removal efficiencies achieved by MBR treatment ~~or~~ and in the case of MBR coupled with PAC/GAC in order to highlight the contribution of the AC for many MPs. Then the analysis refers to MP removal efficiencies and concentrations in the final effluent, with regard to the configurations reported in Table 1 and considering different PAC dosages and the volume of wastewater treated in the GAC column, expressed in terms of number of empty bed volumes (EBVs). The discussion which follows deals with the influence of the main factors affecting MP removal: MP properties, AC characteristics and dosage frequency and mode, and operational conditions in the different configurations (sludge retention time SRT, hydraulic retention time HRT, temperature T, PAC contact time, effluent dissolved organic matter DOM, empty bed contact time, EBCT). The study also explores other effects of AC on removal of macropollutants, mitigation of membrane fouling and MBR sludge characteristics. It then concludes with the identification of the fields requiring further research and investigations.

3 Identification of the studies for the qualitative and quantitative analysis

The present systematic review has been developed following the PRISMA guidelines (Moher et al., 2009), a protocol established in 2009 by international experts that defines the steps to follow to obtain a systematic review on a specific topic. The collection of peer reviewed papers was obtained through Scopus, by the key words "MBR" OR "membrane bioreactor" OR "membrane reactor" AND "activated carbon" OR "AC" and following the eligibility criteria discussed in the Supplementary Material (section S1 and Fig. S1). As a result of this process, a collection of 64 peer reviewed papers, published between 2009 and 2020, was defined including studies presenting and discussing the new trends in the enhancement of the

performance of MBR in combination with AC, in terms of removal efficiency of macro- (BOD_5, COD, nitrogen compounds and phosphorus compounds) and micro-pollutants, and fouling reduction and control (Figure S1). Based on these studies and following the PRISMA guidelines, a qualitative synthesis was carried out. Then a further refinement was made, leading to the identification of 26 records on which basis a quantitative synthesis was carried out referring to the removal of MPs in MBR coupled AC (PAC or GAC). A few studies (4) referring to CAS where AC was present were included as they provided useful insights into the analysis of MP removal, as will be discussed later. More details about the process followed to define the collection of papers to be included in the review can be found in the Supplementary Material.

3.1 Quality assurance of the literature data

The studies included in this review had to provide a clear description of the plant configuration and report information on sampling (mode and frequency of sampling and sampled matrices) and the adopted analytical methods of the investigated micropollutants. There had to be sufficient collected data to support the study discussion. Moreover, the studies had to state at which plant scale (lab, pilot or full) the investigations were carried out, and also had to give details on the biological stage (i.e. design parameters and operational conditions), feeding type (real, synthetic or spiked) and mode (continuous or batch), as well as the duration of the investigation in order to evaluate the level of saturation of the AC during the sampling campaigns. As to AC, they had to report the carbon types and main characteristics (see Table 3). Finally, in the case of AC used as a PT, the study had to provide details of a further treatment (often a membrane unit) inserted in the configuration in order to guarantee the separation between treated effluent and AC residues. This separation step is generally adopted in the case of a PAC unit, but in some cases it was placed after a GAC column (Sbardella et al., 2018).

Table S2 (Excel) in the supplementary material collects all the information and shows the main issues addressed in the 26 selected studies providing MP concentrations and removal efficiencies. The remaining 38 out of the preselected 64 papers were included in this review as they contributed to explaining the behaviour of the AC that was added in the secondary or polishing treatment.

Some investigations dealt with the removal mechanisms of specific MPs and often used deionised, modelled water spiked with the key pollutants at the desired concentration (such as Lee et al., 2009). These studies were included in this review as they provide interesting analysis and useful considerations on the removal mechanisms of the investigated

compounds. However, the removal achieved is not included in the graphs reported in this paper as they refer to deionised water and no matrix effect was considered. Investigations referring to synthetic water (see Table S2) were included only if details on the characteristics of the water matrix were clearly reported.

Finally, if the concentration of MP in the investigations was found to be less than its limit of quantification (LOQ), half of the LOQ was assumed. If its concentration was found to be less than its limit of detection (LOD), it was assumed equal to the corresponding LOD. If the authors reported a removal efficiency equal to 100% and they did not provide the LOQ or LOD values, it was assumed that the effluent concentration was equal to 10^{-4} □g/L. Removal efficiencies were not considered in the cases in which MP influent concentrations were found to be less than the corresponding LOQ.

3.2 Main characteristics of the reviewed studies

The reviewed studies were carried out in Australia (5), Spain (5), Switzerland (3), Netherlands (3), China (2), Canada (2), Germany (2), Belgium (1), Sweden (1), United Kingdom (1) and Saudi Arabia (1). The plant configurations are schematically reported in Table 1, together with a brief description of the system and the corresponding references. The studies included lab (46%), pilot (42%) and full-scale plants (12%). In 50% of the studies, the feeding was synthetic wastewater, resulting from the addition of specific compounds miming the matrix effect (the composition is provided), and in 50% it was real wastewater. Out of these, only one study spiked MPs into the real wastewater (Remy et al., 2012). Regarding the real wastewater, 69% was urban and 31% hospital effluent (Itzel et al., 2018), (Langenhoff et al., 2013), (Kovalova et al., 2013b), (Paulus et al., 2019). The feeding was continuous in all the studies with the exception of (Alvarino et al., 2017; Serrano et al., 2011).

Among the selected 26 papers dealing with the occurrence and removal of MPs, some reported details of very complex experimental campaigns and it was possible to identify different investigations in the same paper. An investigation consists of an experimental campaign referring to a specific treatment configuration/scenario (MBR equipped with MF or UF membranes, coupled with PAC or GAC), under defined conditions (for instance dosage of PAC or empty bed contact time in GAC column). According to this definition, there was a total of 46 investigations regarding the selected records: their details are reported in Table S2 on the line *Investigations on micropollutants*.

3.3 Configurations included in the review

The reviewed configurations belong to three main groups depending on the treatment stage in which AC is present and on AC type: PAC in the bioreactor (configurations I and II in Table

1); PAC in a post treatment (configurations III–V in Table 1); GAC in a post treatment (packed column, configurations VI-VIII in Table 1).

Submerged (I) and side stream (II) MBRs are separated, but the collected results are presented together.

If PAC is used in the PT, it is added in a contact tank receiving the biological effluent to be treated and dispersed in it (Kovalova et al., 2013b; Margot et al., 2013). Sufficient mixing is required to guarantee homogenous conditions. An additional filter is requested in order to retain the AC powder: the UF membrane unit is always equipped after the PAC contact tank (configurations III-V). PAC retained in this unit can be withdrawn (III and IV) or recycled back to the biological reactor (V). If GAC is used as a PT, its granules are packed in a column which is fed and crossed by the biological effluent. In order to clean the GAC filter and remove the retentate, a backwash is planned and periodically carried out (Baresel et al., 2019). A UF unit after the GAC column was found only in one study (VIII). Despite the main aim of this review being the analysis of the performance in a hybrid MBR, four studies referring to CAS coupled with AC (configurations III, VII and VIII) were also included. Two studies explore the effect of a PAC unit after a CAS (Löwenberg et al., 2014; Margot et al., 2013) and another two explore the combination of a CAS with GAC ((Grover et al., 2011; Sbardella et al., 2018). The reason for their inclusion is that they further investigate the removal of MPs and provide useful information to also explain MP removal in a–hybrid MBR. As reported in Table S2, in 26 out of the 46 investigations, PAC was added in the bioreactor, in 7 PAC was used as a PT and in 13 GAC was used as a PT. In the following sections, it was assumed that if the powder of activated carbon is added in the biological reactor (MBR or CAS), the system is reported as (MBR+PAC) or (CAS+PAC), whereas, if activated carbon is used in a separate tank, the configuration will be represented with these symbols: MBR→PAC or GAC; CAS→PAC or GAC.

It is important to remark that the operation, in case AC is added in the bioreactor or AC acts as a PT by means of PAC or GAC, is regulated by different parameters depending on the three main configuration groups. In MBR+PAC they are (i) the *hydraulic retention time (HRT)* of the wastewater in the bioreactor which must be long enough to guarantee MP transfer from the liquid phase to the PAC surface or its absorption in the floc; (*ii*) *the sludge retention time* (SRT) which must be long enough to promote the development of different species of microorganisms able to degrade different MPs, (iii) the *AC retention time* in the bioreactor which is the time AC spends in the tank before its disposal or before it leaves the bioreactor embedded into the floc (in general it is ≥ SRT); finally (*iv*) the *AC working age*

which measures the time since it was added in the system (an indirect measure of AC saturation) which is ≤ AC retention time. In PAC acting as a PT, the specific parameters influencing its performance are: the *HRT* of the (waste)water in the PAC contact tank; (ii) the *AC retention time* in the tank that is the time AC stays in the tank before its withdrawal; and (*iii*) the AC *working age*. In GAC acting as a PT, parameters defining its behaviour are: (*i*) the *HRT* of the (waste)water within the AC column which is measured by the empty bed contact time (EBCT); (*ii*) the *filtration velocity* v_f which is the ratio between the influent flow rate and the surface area of the GAC filter and (*iii*) the *working age* which depends on the EBV. EBCT has to be set in order to guarantee the time for the MPs transfer from the bulk phase to the GAC surface and also inside its grain. According to the suggested design parameters in well-known manuals (among them (Metcalf & Eddy, 2014)), EBCT should be at least 5–30 min and v_f 5–15 m/h. EBCT may be replaced by the *effective contact time* that is defined as the product of EBCT and the bed porosity. These specific parameters are reported for each study In Table S2, together with many other details on the investigations. Finally, the period of investigations on micropollutant removal in hybrid MBRs with PAC or GAC varied between 9 days (Kovalova et al., 2013b)(Wei et al., 2016) and 3 years (Grover et al., 2011). Out of the 46 investigations, only a few provided detailed trends of the removal efficiencies in the presence of AC over time. These included (Nguyen et al., 2013a)(Serrano et al., 2011)(Alvarino et al., 2017, 2016; Li et al., 2011; Lipp et al., 2012).

Table 1

3.4 The selected compounds

The analysed micropollutants included 179 compounds belonging to 30 classes (Table 2). The compounds in italics and with an asterisk were investigated, but they were never detected. As a result, 163 compounds are included in the graphs and belong to 28 classes (those with an acronym in Table 2).

Table 2.

The class of calcium channel blockers (M) was included in the list in Table 2 as the compound amlodipine was found in raw wastewater (Baresel et al., 2019). It was removed below its LOD in the MBR and for this reason it does not appear in any figure resulting in the investigated configuration MBR→GAC.

3.5 Activated carbon used in the investigations

The activated carbon adopted in the reviewed studies was in most cases in powder form (PAC) and in a few studies in granules (GAC). It was generally supplied by: Norit, Chemviron, Desotec, Sigma Aldrich and ChiemiVall, as reported in Table S2. The size generally ranges were < 50 □m for PAC and 100–2,400 □m for GAC, in accordance with Metcalf and Eddy (2006), only (Sbardella et al., 2018) adopted a GAC with a higher size range (2,360–4,750 mm). Among the selected 66 papers, it was also found that sometimes AC up to 300 □m was considered PAC ((Ng et al., 2013)(Yang et al., 2019)(Zhang et al., 2017)). A few authors provide more details about the particle size distribution of the adopted AC ((Ng et al., 2013)(El Gamal et al., 2018)). Many studies also considered the influence and role of pore size (Alves et al., 2018), which was classified, in accordance with IUPAC (Rouquerol et al., 1994), in micropores (diameter < 2 nm), mesopores (diameter between 2 nm and 50 nm) and macropores (diameter > 50 nm).

The main characteristics of AC are reported in Table 3. The most important ones are Brunauer–Emmett–Teller *BET specific surface area* as it is a measurement of the potential surface area available for promoting the different removal mechanisms which will be discussed later on; *iodine number* which is a measure of the pore volume available in the AC mass; *pore diameter* defining the size of the particles which can enter the porous structure of the grain; and the *apparent* or *bulk density*, that is the mass of AC contained in a unit volume (including particle, inter-particle void and internal pore volume).

In addition, the point of zero surface charge (pH_{PZC}) is another important characteristic, reported in some study (Alves et al., 2018; De Ridder et al., 2011; Kovalova et al., 2013b, 2013a), which defines the pH at which there are as many positively charged functional groups as negatively charged functional groups on the AC surface (pH_{PZC} between 6.5 and 8 indicating that their surface is slightly positively charged or negatively charged at neutral pH, (De Ridder et al., 2011)). At wastewater pH below pH_{PZC}, the carbon surface is mostly positively charged and, above the surface, it is mostly negative charged. It is important to know this threshold, as the adsorption process is most effective for uncharged apolar adsorbates (Alves et al., 2018).

Only one study (Alves et al., 2018) investigated the influence of the activation type (by steam or by chemicals) of the carbon and compared the results at lab level and (Choi et al., 2005; Paredes et al., 2018) explored the effect of the GAC type on removal efficiencies and GAC lifetime.

Table 3

On the basis of origin and activation mechanism, ACs present a high heterogeneity (Benstoem et al., 2017). However, it is worth noting that the selection of virgin and reactivated carbon and the operation time may influence the adsorption capacity as their characteristics may change over time (Benstoem et al., 2017; Choi et al., 2005).

In the investigations with PAC added in the bioreactor, the dosage was between 0.004 g/L (Remy et al., 2012) and 20 g/L (Asif et al., 2020). In the following analysis the dosages considered are discretized as: < 0.05 g/L, 0.051 g/L; 0.25 g/L, 0.5 g/L; 0.75 g/L, 1–2 g/L and 20 g/L. The highest dosage (20 g/L) was selected on the basis of the batch test carried out by (Asif et al., 2020). It had to guarantee a very high removal (> 90%) of soluble microbial products (SMP) in the biological tank and under unsaturated conditions for PAC over the whole investigation.

As to the GAC column, the removal efficiency is often expressed as a function of the number of empty bed volumes (EBV), defined as the ratio between the treated (waste)water volume and the GAC column volume.

4 The role of activated carbon in the removal of micropollutants

Activated carbon may be added in the bioreactor or it can be used as a PT fed by the secondary effluent or the permeate, as reported in Table 1. Its presence favours similar removal mechanisms for the micropollutants in the case of granules (GAC) or powder (PAC). As shown in Table 3, PAC and GAC are characterised by a high specific surface (m^2/g) due to the presence of micro-, meso- and macropores. The internal structure of a grain, without taking into consideration its specific size, is reproduced in Figure 1A. On its whole surface there is a high number of *active* sites where compounds (micro- and macro-pollutants) occurring in the wastewater can bind, depending on their affinity with the AC surface, and thus they are removed from the liquid phase via sorption mechanisms. Pores in the granule or in the powder are of different sizes resulting in different thresholds for the size of the molecules which can penetrate and then adsorb on the internal surface of the AC grain.

Micropollutant affinity towards an AC is strictly correlated to the physical and chemical characteristics of the AC (Section 3.2.3), namely pore size and texture, surface functional groups (Figure 2C) and charge, and mineral matter content (Alves et al., 2018; Choi et al., 2005; Fuente et al., 2003; Kovalova et al., 2013b). Micropores are directly responsible for MP adsorption (El Gamal et al., 2018) as shown in Figure 1B.

Adsorption is expected to decrease over time due to a gradual saturation of the active sites during operation (Choi et al., 2005). Dissolved organic matter (DOM), and in particular the

fraction of low molecular weight organics (see section 6.1.8), if present in the liquid phase in contact with AC, tends to adsorb on the AC surface (Filloux et al., 2012). Organic particles may enter the macropores, thus they may represent a barrier for the MPs in their movement to reach the active sites of meso- and micropores. DOM and MPs are numerically present at different levels. In this context, (Rattier et al., 2012) found that DOM acts as a strong competitor when it occurs 10^3–10^6 times higher than MPs. In the presence of DOM in the liquid phase (wastewater under treatment), microorganisms may develop on the AC surface area and macropores (Alves et al., 2018), promoting the growth of a biofilm, thus favouring biodegradation processes due to microorganism metabolic reactions. The AC thus becomes *biologically activated carbon* (BAC) (Figure 1C). The MP biodegradation processes are enhanced here due to the development of a more specialised biomass, and the coexistence of aerobic and anoxic zones in this biofilm (Alvarino et al., 2016). MPs occurring in the wastewater may be sorbed by two mechanisms: *adsorption* due to electrostatic interactions between MP charged groups and the oppositely charged biofilm or AC surface, and *absorption* into the biofilm stratum due to MP hydrophobic interactions of the aliphatic and aromatic groups with the lipophilic cell membrane of the microorganisms or the lipid fractions of the suspended solids. Then some may biodegrade by means of microorganisms in the biofilm, transform and even mineralise; others may remain as they are (Baresel et al., 2019) (Figure 1).

Figure 1

When AC is added in the bioreactor, it comes into contact with the flocs (activated sludge): some AC particles are incorporated within them, others are suspended within the liquid phase, depending on the AC added quantity (Ng et al., 2013) (Remy et al., 2010) (Figure 2A). Sludge flocs are dynamic systems where incorporated AC particles may be covered by the biofilm becoming BAC or they may have their surface partially free (Figure 2B). In this last case, MPs may directly adsorb on the AC surface. If the AC is covered by the biofilm, MPs may be absorbed in the biofilm, desorbed from it and adsorbed on the smallest AC pores. Bacteria can only colonise macropores due to size exclusion. Extracellular polymeric substances (EPS) instead can also enter into meso- and micropores and thus act as a catalyst for the biodegradation processes of MPs which manage to reach the surface of these pores and attach to it (Alves et al., 2018).

Figure 2.

If AC acts as a PT, by PAC (as reported in Pills, 2012) or GAC (Sbardella et al., 2018), the development of the biofilm on its surface is still possible: DOM may be retained by the granules (Seo et al., 1996; Sun et al., 2020) and, over time, it may promote the growth of an autochthonous biomass (Sbardella et al., 2018). Sorption and biodegradation are complementary mechanisms that extend the AC life. During backwashing operations of the GAC filter, some MPs could be detached from the filter and found in the backwash water (Baresel et al., 2019). At long operating times, mature or aged biofilm developed on the AC surface may detach giving rise to the biological regeneration process. This cleans the AC surface, and the AC active sites are now free for MP adsorption even at long operating times. The regeneration is not able to create the original conditions and AC replenishment may become necessary to guarantee optimal operating conditions.

To sum up, MP removal mechanisms are the results of continuous interactions among MPs and AC particles, biofilm and organic matter. For this reason, BAC has to be considered a dynamic system where MP sorption and biodegradation occur simultaneously (El Gamal et al., 2018).

4.1 Common parameters and coefficients used in predicting MP removal

The sorption potential of an MP onto an AC is given by its solid water distribution coefficient K_d defined by eq. 1:

$$K_d = \frac{c_{sorbed}}{c_{dissolved}} \text{ (eq. 1)}$$

where c_{sorbed} is the concentration of the compound of interest sorbed on the AC (□g/kg), $c_{dissolved}$ is the MP concentration in the liquid (□g/L). K_d is expressed in L/kg. It is strictly correlated to the nature of the adsorbent (case specific). A rapid look at the literature on MP sorption on AC shows that experimental values are very scarce (Yang et al., 2012).

As remarked in (Dickenson and Drewes, 2010; Mailler et al., 2015; McArdell et al., 2011; Rattier et al., 2012), MP sorption onto the surface of a particulate matter (activated sludge or AC) is due to MP hydrophobicity (absorption) and to electrostatic interactions between positively charged compounds and negatively charged solid surface (adsorption).

The octanol water distribution coefficient D_{ow} can be used to predict its behaviour.

It is a modification of the octanol-water partition coefficient (K_{ow} defined by eq. 2) accounting for ionisation of the compound (for non-ionisable compounds D_{ow} and K_{ow} have the same value) and it also considers attraction by the solid (correlated to pK_a). Equations 3 and 4 corresponds to the correlations between K_{ow} and D_{ow} for acidic and basic compounds respectively.

$$K_{ow} \equiv \frac{\text{concentration in } n\text{−octanol}}{\text{concentration in water}} \text{ (eq. 2)}$$

$$Log\ D_{ow} = Log\ K_{ow} + Log \frac{1}{1 + 10^{pH - pK_a}} \text{ (acidic compound) (eq. 3)}$$

$$Log\ D_{ow} = Log\ K_{ow} + Log \frac{1}{1 + 10^{pK_a - pH}} \text{ (basic compound) (eq. 4)}$$

For neutral compounds Log D_{ow} = Log K_{ow} and for ionic solutes Log D_{ow} < Log K_{ow}
However, even if D_{ow} is corrected for charge (through pK_a), it only reflects how polar the compound is. Adsorbability prediction for charged compounds is more complex, as different mechanisms are involved as it will be better discussed in section 6. Table S1 reports Log K_{ow}, p K_a and Log D_{ow} at different pH as well as charge at pH=7 for the different compounds included in this study.

As to biodegradation, the kinetic constant k_{biol} is influenced by the operational conditions set in the bioreactor (mainly biomass concentration and type, HRT, and temperature), MP characteristics, and the availability or limitation of substrates which define the type of biodegradation process (by metabolism or cometabolism) (Alvarino et al., 2018). These considerations explain the reasons why predictions are quite difficult and experimental data are often not in agreement with such data.

5 Results

Collected data provided by the investigations included in this review were processed in order to compare the MP removal achieved by the selected configurations in Table 1, at different AC dosages and under different operational conditions. Moreover, AC working age and behaviour over time were also explored and discussed. The first analysis carried out refers to the contribution of AC in removing MPs in the case of PAC added in the bioreactor (Figure 3) or GAC used as a PT (Figure 4) in comparison with the removal achieved by a biological treatment alone. It was not possible to compare MP removal achieved by the biological step alone or in the case of the biological step being followed by a PAC unit due to lack of corresponding values in the biological stage (Kovalova et al., 2013b; Lipp et al., 2012; Löwenberg et al., 2014; Margot et al., 2013).

In Figures 3 and 4, lower case letters at the top of the graph correspond to the specific studies reported below the figure. In some cases, the same compound has been the subject of more than one investigation (for instance, in Figure 3, diclofenac was investigated in 6 studies called: *a, b, d, f, g* and *i*). Compounds belonging to a class are grouped together and the name of the class is reported in upper case (according to Table 2) at the bottom of the graph. Finally, the separate grid shows when the micropollutant was released. This means that negative removal efficiencies were reported in the reviewed papers, occurring in MBR alone (more often) and/or in MBR combined with AC (only for carbamazepine, (Li et al., 2011)).

Figures 3 and 4 do not correlate removal efficiencies with specific operational conditions and configurations: the hybrid MBR is considered a *black box* and the details regarding quantity of added PAC or operational conditions referring to PAC or GAC are not reported, or when the PAC is added (in the anoxic or in the aerobic compartment): they will be discussed in section 6.

In more detail, Figure 3 refers to the removal achieved for 48 compounds belonging to 13 classes in MBR and (MBR+PAC). It emerges that the presence of AC added in the biological tank improves the removal of most of the compounds: it occurred in 79 out of the 108 reported cases. In 13 of the remaining 29 cases, MP removal did not improve and, according to the authors, this was due to the fact that the compound was almost completely removed in MBR and, due to the presence of AC, the contribution was not relevant (Nguyen et al., 2013a). In the last 16 cases, the MBR presents a higher removal efficiency than the corresponding case of MBR+PAC. Details of these analyses are reported in Table S3. Briefly: higher MP removal values found in MBR alone compared to MBR+PAC were related to removal data referring to different AC working age (Alvarino et al., 2017; Nguyen et al., 2013a), different sludge properties resulting in different characteristics of the cake developed against the membrane and this cake filtration performance (Alvarino et al., 2017) and accidental temperature drop (Li et al., 2011). As to Figure 4, it includes 22 compounds belonging to 9 classes and 44 columns. The removal in MBR→GAC was higher in 27 ~~64~~ cases than in MBR alone. In 16 cases, MBR reached almost complete removal efficiencies and the removal efficiency did not increase after the GAC stage. In only one case referring to paracetamol, the trend is not clear.

Table S4 reports further details about this analysis. Due to a lack of data referring to the removal efficiencies for MPs achieved in MBR alone, but only in GAC as a PT, data reported in (Baresel et al., 2019; Grover et al., 2011; Langenhoff et al., 2013; Sbardella et al., 2018) were not included in this figure.

Figure 3 shows that MP release occurred occasionally with the only exception of trimethoprim, which was always released in the investigations by (Serrano et al., 2011). The authors explained this finding by the fact that nitrifier bacteria were absent in the biomass within the MBR and trimethoprim was not degraded by the different species developed in the microbial community. In the other cases, MP release was ascribed to the following causes: changes in operational conditions (for instance a sharp increment of the MP concentration in the influent) (Li et al., 2011), environmental conditions such as a decrement in temperature which strongly affects biological reaction rates (Li et al., 2011); AC saturation (Alvarino et

al., 2016), re-generation of parent compounds starting from the corresponding metabolites or transformation products (for diclofenac and carbamazepine), (Alvarino et al., 2016). Another possible reason, not reported in the reviewed studies, but often remarked in the literature (Verlicchi et al., 2012), is an inappropriate sampling protocol.

These first rough comparisons lead to the consideration that the presence of AC has the potential to improve removal for most compounds. The influence of the main operational parameters will be analysed in detail in section 6.

Figure 3.
Figure 4.

5.1 Removal in MBR+PAC

In order to better investigate the influence of the *amount of PAC added* in the bioreactor, literature data were reported in Figure 5 considering the different PAC dosages, between < 0.05 g/L and 20 g/L of PAC. PAC dosages were classified as: < 0.05 g/L, 0.05-0.1 g/L; 0.25 g/L, 0.5 g/L, 0.75 g/L, 1-2 g/L and 20 g/L. In Figure S2, the same data are reported according to the Authors. Based on the collected data, 43 compounds belonging to 13 different classes were analysed, and the most studied were carbamazepine (31 values), diclofenac (28), naproxen and sulfamethoxazole (27), ibuprofen (26), trimethoprim (24), erythromycin (23), roxithromycin (22), EE2 (21) and E1 (20). The remaining compounds have only 1–6 values of removal efficiency. It emerges that all the compounds can be removed by MBR+PAC, even the most recalcitrant diclofenac and carbamazepine. The variability ranges are 32% to 99% for diclofenac, the highest values were found in (Alvarino et al., 2016), and 15% to 99% for carbamazepine, with the top removal reported in (Alvarino et al., 2017). At the lowest doses of PAC (< 0.05 g/L), the removal efficiency is at least 60% with the only exception of sulfamethoxazole (it needs at least 0.25 g/L to achieve 60% removal). The high dosage of 20 g/L in (Asif et al., 2020) was selected in order to guarantee a homogeneous integration of PAC and sludge and to achieve the best rheological properties of the sludge.

An analysis of the collected data highlights that the addition of PAC as low as 0.1 g/L is sufficient to achieve a removal of 80% for 34 out of the 37 compounds which were investigated in this range of PAC addition.

Figure 5.
Data from: (Alvarino et al., 2017, 2016; Asif et al., 2020; Echevarría et al., 2019; Li et al., 2011; Nguyen et al., 2013a; Remy et al., 2012; Serrano et al., 2011; Yang et al., 2012; Yu et al., 2014)

PAC addition in the MBR leads to a relevant increment in PFOS and PFOA removal (Figure 3): from < 7% in the MBR to the range 68% to 94% in the MBR+PAC, depending on the concentration of AC and the compound (Yu et al., 2014). Their removal is only due to adsorption on PAC and 0.08 g/L seems to be enough to reach 80% of removal. The Authors underline that the expected removal with the addition of PAC should be much higher, especially at the highest PAC dosages, but probably because of fouling due to sludge and DOM, the available PAC surface for PFOA and PFOS adsorption was greatly reduced and this was more evident for PFOS, the compound with higher sorption potential (higher D_{ow}, see Table S1). For the most investigated compounds (diclofenac, sulfamethoxazole and carbamazepine), the addition of PAC leads to an increment in removal efficiency, despite its value varying in a range greater than 50%. This leads to the conclusion that PAC added in the MBR does not guarantee a minimum removal for the compounds due to many factors that influence their behaviour, which will be discussed in section 6.

5.2 Removal when AC is used as a post treatment

An analysis of the removal efficiencies achieved when PAC is used as a post treatment is reported in Figure 6: PAC treatment follows the biological step consisting of a CAS (Löwenberg et al., 2014; Margot et al., 2013) or an MBR (Kovalova et al., 2013b). The tested doses were < 0.05 g/L for CAS and MBR and 1-2 g/L for CAS. With regard to the first interval, the tested dosages were 0.008, 0.023 and 0.043 g/L for MBR→PAC (light blue square in Figure 6) and 0.0171 g/L for CAS→PAC (dark square in Figure 6). Referring to the light blue square values, the wide variability emerging from Fig. 6 is strictly correlated to the different dosages. An in-depth analysis is available in the report (McArdell et al., 2011) as well as in (Kovalova et al., 2013b).

Removal values of compounds in MBR→PAC < 20% were found at the lowest doses of PAC (0.008 g/L). This was the case for all the contrast media (class N) with the only exception of iopromide which exhibited a removal of 47% already at these dosage conditions. Diatrizoate and ioxitalamic acid were always poorly removed: between 1% and 18% at the different tested doses. Moreover, it was found that poor removal (21% to 35%) is achieved for all contrast media in MBR alone ((Margot et al., 2013) data not shown) and PAC addition may remove them, depending on the added dose. Fluctuations in the removal efficiencies of such recalcitrant compounds also leading to negative values (not shown) may be ascribed to variations in their influent concentrations (Lipp et al., 2012) and to a sampling mode that implies the analysis of the grab or composite samples taken not considering the HRT of the monitored treatment stage (Verlicchi et al., 2012). It emerges that a higher dose is not able to

enhance the removal achieved for diclofenac, sulfamethoxazole, mecoprop and carbamazepine. At the same dose of PAC as a PT after a CAS or an MBR, the removal achieved after an MBR is higher with respect to the removal achieved after a CAS for diclofenac (95% to 99% versus 82% to 85%) and carbamazepine (99% versus 90% to 99%), lower for sulfamethoxazole (2% to 60% versus 58% to 64%) and partially overlapped in the case of benzotriazole (68% to 92% versus 90% to 92%). This can be ascribed to the interactions between the organic matter and the AC surface, which are more relevant in the case of CAS effluent due to its higher concentration with respect to MBR permeate. In these configurations, there was a higher number of compounds with a variability of more than 50% in their removal efficiency compared to configurations I and II (Figure 6) where only three compounds presented such a variability range.

Figure 6.
Data from: (Kovalova et al., 2013b; Löwenberg et al., 2014; Margot et al., 2013)

Figure 7 refers to MP removal efficiencies in a GAC column acting as a PT, after the biological step at different empty bed volumes (EBV), that is during the GAC working period. They varied between < 1,000 EBV (Nguyen et al., 2013b, 2012) and 60,000 EBV (Baresel et al., 2019). Some investigations did not report the EBV correlated to the removal values and thus their data are not included in Figure 7 (Grover et al., 2011; Itzel et al., 2018; Langenhoff et al., 2013; Paulus et al., 2019). On the contrary, all the collected data on removal efficiencies in a polishing GAC unit are reported in Figure S3, grouped according to the Authors. It emerges that for most investigated compounds the removal efficiencies vary greatly. The smallest variability intervals were found for bisphenol A (6%, between 77% and 83%), ciprofloxacin (23%, between 63% and 83%), and 4-n-nonylphenol and 4-tert-butylphenol (25% respectively 50% to 75% and 74% to 99%).The widest interval was found for diclofenac (3% to 99%), with the lowest value found in (Nguyen et al., 2013b) and the highest values collected in (Paredes et al., 2018) and (Baresel et al., 2019). The extremely low removal was ascribed to the saturation of the GAC column, whereas the highest removal values may be ascribed to the biological regeneration within the BAC which thus allowed a high and continuous MP removal from the real wastewater, even at high EBVs. As diclofenac is poorly removed in biological processes (20% to 30% as in Figure 4), the contribution of the GAC column in its removal is fundamental. The removal achieved with the GAC filtration is related to MP nature, its biodegradability and sorption potential, the degree of

saturation level of the AC filter, the EBCT, as well as MP concentration in the GAC influent. If a compound is highly removed in the bioreactor, the resulting concentration in the treated effluent is low. In this case, MP removal efficiencies are around 40% to 50% in the GAC column are still to be considered very good as they lead to a very high overall removal. This is the case for ibuprofen, paracetamol, E3, 4-tert-octylphenol, 4-tert-butylphenol and 4-n-nonylphenol. When MP removal in the bioreactor is moderate and also variable in a wide range (20% to 70%), it emerges that the GAC can have two different behaviours, which mainly depend on the nature of the compound. GAC can exhibit a fairly constant removal efficiency up to its saturation (ketoprofen); on the other hand, it seems that GAC performance may adapt to the variations in the permeate concentration. This was the case for metronidazole for which GAC was able to guarantee a very high removal efficiency leading to an overall removal between 86% and 99%, as shown in Figure 4 (Nguyen et al., 2013b). This issue will be discussed later and compared with recent literature findings. In the case of compounds with very low removal efficiencies in the bioreactor, GAC may greatly contribute to their removal and its presence is essential for assuring a good removal of such recalcitrant compounds. If a decrement occurs, it may be correlated to GAC saturation conditions (fenoprop, carbamazepine and diclofenac). If biological regeneration occurs (see section 4), MPs may still be removed by adsorption. This explains the behaviour of atenolol, metoprolol and propranolol, the antibiotic trimethoprim and the diuretic hydrochlorothiazide, and also diclofenac, which maintain a medium-high removal efficiency for a long working time (Baresel et al., 2019; Sbardella et al., 2018). In the case of GAC saturation, biodegradable compounds absorbed in PAC or adsorbed in GAC, may still undergo biodegradation processes which maintain a good removal efficiency at long operation times (azithromycin, ciprofloxacin, ofloxacin, and sulfamethoxazole) (Sbardella et al., 2018).

Figure 7.

Data from: (Baresel et al., 2019; Nguyen et al., 2013b, 2012; Paredes et al., 2018; Sbardella et al., 2018).

5.3 MP concentrations in MBR+PAC effluent

Figure 8 and Figure 9 refer to MP concentrations in the effluent from an (MBR+PAC) system included in the review. The different symbols used for these effluent quality data depend on the value of the corresponding biological stage influent. Ranges were set for the influent concentrations: 0.01-0.1 □g/L, 0.1-0.5 □g/L, 0.5-1 □g/L, 1-25 □g/L, 100-120 □g/L and 750

□g/L. This discretisation was defined on the basis of the collected literature data and there is no constant interval width for this reason. Data reported in Figures 8 and 9 refer to different types of MBR (in particular they could include UF or MF membrane units, different microbial community species, for instance the presence of nitrifier bacteria as discussed in (Alvarino et al., 2017), different AC dosages in the reactor, different AC ages, different influent characteristics in terms of micro- and macropollutants. They thus provide ranges of effluent concentrations corresponding to different operational conditions in the treatment systems. For this, the analysis of the reported trends requires great caution.

MP concentrations lower than 0.01 □g/L correspond to a very good quality of the effluent. They refer to compounds which have a high sorption potential ($\log D_{ow} > 3$, as for E2□), or are highly degradable (caffeine), or have a low influent concentration (naproxen). Additionally, they refer to high PAC dosages (naproxen, paracetamol, salicylic acid and oxytetracycline, azithromycin, caffeine) (Asif et al., 2020)(Alvarino et al., 2017) or to fresh PAC (erythromycin, roxithromycin, sulfamethoxazole, fluoxetine) (Alvarino et al., 2016)(Alvarino et al., 2017).

The highest effluent concentrations correspond to the highest influent values or ranges of concentrations: this was the case for sulfamethoxazole (Li et al., 2011) (in Figure 8), PFOA and PFAS (Yu et al., 2014) and carbamazepine (Li et al., 2011) (in Figure 9). There is an exception: carbamazepine in Fig. 9 has an effluent concentration similar to the influent one (around 22 □g/L). According to the authors (Serrano et al., 2011), this might be ascribed to the saturation of the AC after three months of continuous operations. The release of carbamazepine (see Figure 3) reported in (Li et al., 2011) was related to an accidental low temperature which may have reduced the kinetics of the biological processes and the transfer of the MP from the solid (sludge or AC) to the liquid phase. The effluent concentration increased to 190 mg/L from 100 mg/L in the influent. Paracetamol (Figure 8), an easily degradable compound, was found at a very low concentration also with an influent concentration equal to 118 □g/L (Echevarría et al., 2019) and with an AC dosage in the range 0.025–0.050 g/L.

Figure 8. Data from: (Alvarino et al., 2017, 2016; Asif et al., 2020; Echevarría et al., 2019; Li et al., 2011; Nguyen et al., 2013a; Serrano et al., 2011; Yang et al., 2012)

Figure 9.

Data from: (Alvarino et al., 2017, 2016; Asif et al., 2020; Echevarría et al., 2019; Li et al., 2011; Nguyen et al., 2013a; Remy et al., 2012; Serrano et al., 2011; Yu et al., 2014)

On the other hand, diazepam (Figure 9), a poorly degradable compound, was found in the effluent at 0.1–11 □g/L with the corresponding influent in the range 10–25 □g/L (Serrano et al., 2011). The highest effluent concentrations are due to PAC saturation (Alvarino et al., 2016).

If a threshold is set equal to 1 □g/L for the effluent concentration of an AC treatment, out of the 48 reported micropollutants in Figures 8 and 9, 32 compounds are always below such threshold, and 16 compounds are at least one value above. If the threshold is set at 0.1 mg/L, the compounds with at least one value above it become 39 out of 48. This means that most of the selected MPs may occur in the MBR+PAC permeate in the range 0.1-1 mg/L.

5.4 MP concentrations in the effluent of an AC stage (post treatment)

Figure S4 and Figure S5 refer to the effluent quality if PAC or GAC are used as a PT. Reported data are related to the influent concentrations and to PAC dosage or GAC EBV. Compounds in light pink (64) refer only to PAC, those in light grey (22) only to GAC, and the remaining 29 to both AC types. It emerges that the maximum concentrations in the effluent were found in general for PAC treatment, with the contrast media (class N) being the compounds exhibiting the highest concentrations (10–2,750 mg/L) based on the findings by (Kovalova et al., 2013b). In discussing these data, it is important to remark that they refer to high influent concentrations (Figure 9), and to investigations which exhibited an average (good) removal of around 60% (Figure 6). Limiting the attention to the 29 common compounds (Figure S6), and to the applied conditions (see Figures S4 and S5), it seems that the quality of a PAC unit effluent is better for analgesics/anti-inflammatories, hormones and carbamazepine, whereas in case of a GAC column effluent the quality is better for antibiotics, beta-blockers and diatrizoate. A reduction in the concentrations is more evident for those compounds occurring at higher influent concentrations, underlining that the observed removal efficiencies (Figure 6 and Figure 7) are strictly dependant on the influent concentrations, as also discussed for other treatments, such as the biological stage (Verlicchi et al., 2012).

If a threshold is set at 1 mg/L, out of the 115 compounds analysed, 22 have at least one value exceeding it (20%). They are mainly analgesics, anti-inflammatories and contrast media.

A comparison was carried out between the quality in the case of MBR+PAC (Figures 8 and 9) and MBR→ PAC with regard to the most common investigated compounds: sulfamethoxazole, trimethoprim, carbamazepine and metronidazole. The collected concentrations in MBR+PAC permeate were obtained by an addition of 0.025-1 g/L of PAC in the bioreactor for sulfamethoxazole, trimetroprim and carbamazepine and 0.1 g/L and 0.5

g/L for metronidazole and those referring to the PT unit effluent by an addition of 0.008-2 g/L for all the compounds. It was found that the concentrations of sulfamethoxazole, trimethoprim and carbamazepine are lower when AC acts as a PT, and for metronidazole, the variability ranges of the effluent concentrations are similar in both cases.

Ciprofloxacin shows very good removal in PAC as a PT and in the case of influent concentrations around 15 mg/L.

5.5 Further results

A few studies investigated or estimated the mass load of micropollutants sorbed onto the activated carbon and the activated sludge, with different dosages of PAC in the bioreactor in long-term investigations: PFOS and PFOA in (Yu et al., 2014), and E2 and EE2 in (Yang et al., 2012). (Yang et al., 2012) found that the main contribution due to the presence of PAC is in a greater sorption percentage of the investigated compounds, whereas the impact on biodegradation is quite modest, with the k_{biol} being quite similar (for E2 it was 8.38 1/d in MBR and 9 1/d in MBR+PAC, for EE2 it was 4.41 1/d in MBR and 4.8 1/d in MBR+PAC). (Alvarino et al., 2016) stated that PAC addition leads to an enhancement in the biotransformation for some MPs mainly for those exhibiting moderate kinetics.

As to K_d, they found that the presence of PAC greatly improves the adsorption of EE2, which is more hydrophobic than E2: its K_d in MBR sludge was 1.431 L/gTSS whereas in MBR+PAC sludge it was equal to 4.123 L/gTSS. As to E2, its K_d was 0.916 L/g TSS in MBR sludge and 1.671 L/gTSS in MBR+PAC sludge. As a consequence, the enhanced sorption capacity in MBR+PAC sludge could increase the amount of EE2 and E2 adsorbed onto sludge.

6 Discussion

The potential of AC in removing MPs from wastewater prompted specific investigations on adsorption batch tests under controlled conditions (e.g. aqueous solutions and synthetic water with a simulated matrix effect) (de Ridder et al., 2010; Dickenson and Drewes, 2010). However, removal mechanisms of MPs in hybrid MBRs are not limited to adsorption processes as described in section 4.

AC and MP structure and properties, wastewater composition, and operational conditions strongly influence the overall removal of MPs in MBR coupled with AC. At the same time, AC presence can influence MP fate during treatment, change sludge properties and also have an effect on membrane fouling. These issues will be discussed in the following sections.

6.1 Factors influencing the removal of MPs by the presence of AC

The main factors influencing MP removal are related to compound properties, AC

characteristics and dosage frequency and mode, wastewater composition (namely DOM and its content of large molecules and low molecular weight organics), and treatment operational conditions. The interactions between MP and AC depend on their properties. The extent at which these interactions may develop is related to the available quantity of AC and MP and the conditions under which these interactions occur.

6.1.1 Micropollutant properties

The main properties affecting MP removal mechanisms include molecule charge, Log K_{ow} or better Log D_{ow}, pK_a, molecular size, and specific functional groups within the molecule. Most of these properties are available in Table S1 for the reviewed compounds.

Charge – MP charge is a leading parameter if its removal is due to electrostatic interactions with AC in a hybrid MBR. An analysis of the removal efficiencies of the selected MPs on the basis of their charge (anionic, neutral, zwitterionic and cationic compounds at the operating pH) and Log D_{ow} is reported in Figure S7 referring to a PAC unit acting as a PT. Similar trends were found considering removal in GAC columns as a PT.

It emerges that cationic compounds (including clarithromycin) seem more prone to be removed by AC treatment due to electrostatic interactions between the positively charged surface of the pollutants and the negative surface of the carbon, confirming the findings by (Kovalova et al., 2013b). Cationic compounds seem to be mostly well removed regardless of their other properties (Mailler et al., 2015; Margot et al., 2013). This fact justifies their small removal variability range compared to anionic or neutral ones. In the case of neutral compounds, removal is influenced by hydrophobicity and molecule structure (mainly functional groups that allow H-bonds and π- π bonds) (de Ridder et al., 2010). A significant positive correlation has been found regarding MP removal and Log D_{ow} (Mailler et al., 2015). For anionic compounds, electrostatic repulsion is expected between the AC and MP surface. Although it seems to be a relation between hydrophobicity and removal efficiency in the case of PAC as a PT (see Figure S7), no clear evidence of this phenomenon was found in the literature (Mailler et al., 2015; Margot et al., 2013). However, high MP hydrophilicity can result in low adsorption capacity for charged compounds even when electrostatic interactions are expected between AC and MPs (Kovalova et al., 2013a). Moreover, it seems that saturation is more prone to take place for anionic compounds in wastewater (Mailler et al., 2015).

Log D_{OW} – An analysis of the removal as a function of Log D_{ow} has been carried out by (Alves et al., 2018; Kovalova et al., 2013b; Rattier et al., 2014) for many MPs and they do not show a clear correlation. Referring to neutral compounds, Figure S7 shows that at higher

Log D_{ow} values the removal efficiencies are higher and have a lower variability range. According to (de Ridder et al., 2010) at log D_{ow} greater than 3.7 hydrophobic interactions become the dominant removal mechanism.

Molecular weight – (Alves et al., 2018) found that if AC is added to spiked water, there is a clear correlation between molecular weight and removal efficiency: they stated that the higher the molecular weight, the higher the amount of AC to guarantee the same removal efficiency, confirming that steric hindrance of the large molecules hinders their adsorption rate. This behaviour is more pronounced in the case of hydrophilic compounds, such as iopromide (Log D_{ow}= 0.45).

6.1.2 Characteristics of activated carbon

The main characteristics of AC are reported in section 3.5. Their influence on the removal of selected MPs were investigated by (Alves et al., 2018; Choi et al., 2005; Mailler et al., 2016; Paredes et al., 2018). In particular, (Alves et al., 2018) compared the removal efficiencies for a wide selection of compounds with different types of AC in terms of activation (with steam or chemical), textural properties, chemical properties (related to the functional groups in the outer layer of the grain and in particular to the presence of oxygen surface groups, such as carboxylic, ethers and lactones as reported in Figure 2C), pH-point of zero charge, as well as surface charge at pH=8. They found that in pure water, chemical activated carbons are more prone to attract and bind MPs than steam activated carbons and they guarantee 80% removal at lower doses. (Choi et al., 2005) linked AC characteristics (specific surface area, pore volume and material) to MP adsorption in GAC columns. They found a negative correlation between pore volume and the BET specific surface area; they remarked that the BET specific surface area and pore volume reduce as the operation time increases, their reduction occurs mostly in micro-pores and that MP and DOM adsorbed onto macropores can subsequently cause a micropore blockage. The extent of this reduction depends on the carbon type. According to the investigations by (Fundneider et al., 2021a), a balanced proportion of macro-, meso- and micropores in the GAC improve the MP removal in the presence of DOC, whereas GAC with a high proportion of micropores is more affected by pore blockage due to DOC adsorption leading to a lower MP removal. MP removal is strongly affected by the presence of DOM which may partially cover the AC surface. If an AC is positively charged, it attracts DOM (negatively charged) and thus its surface will have positively and negatively charged zones, thus attracting anionic and cationic MPs respectively (Figure 2). Finally, it was also found that pore volume is more important than specific area and a larger pore volume generally allows a higher removal of MPs (Rossner et al., 2009).

(Mailler et al., 2016) studied the influence on the removal efficiencies of 15 MPs of the physical and characteristics of four PACs. They found that the BET surface area is positively correlated to MP removal. On the other hand, the BET surface area is negatively correlated to bulk density, that is, a high BET surface area corresponded to low bulk densities. As bulk density is an easy-to-measure parameter it could be used as an indicator to select AC.

6.1.3 PAC dosage and losses

PAC dosage seems to be one of the crucial operational parameters regarding the influence on MP removal. Tested dosages were generally defined on the basis of preliminary batch tests aiming at investigating the sorption potential of the specific MP on an AC in pure water. Unfortunately test data regarding adsorption of MPs in the case of PAC added in an MBR did not fit well with the adsorption isotherms (Li et al., 2011; Nguyen et al., 2013b).

PAC was added at the beginning of the investigations (Alvarino et al., 2016) or periodically during the experimental period (Alvarino et al., 2017), (Li et al., 2011). In this last scenario, fresh AC mixes with "older" AC which is partially saturated. It was found that the addition leads to an improvement in the removal of recalcitrant MPs such as carbamazepine and diclofenac and, for this reason, carbamazepine (concentration) was suggested as an indicator of the AC saturation level (Alvarino et al., 2017).

The loss of the *potential* adsorption capacity of the AC is reduced not only by its progressive saturation, but also by its losses from the system by withdrawal of excess sludge or retentate from membrane PT units. PAC addition (replenishment) is thus necessary to maintain its desired concentration in the tank.

6.1.4 Dosage point

In some investigations PAC was added in the anoxic tank (Remy et al., 2012), in others in the aerobic one (Asif et al., 2020), (Echevarría et al., 2019). In (Asif et al., 2020), PAC was added in the aerobic compartment of the anoxic/aerobic side stream MBR and due to sludge recirculation a fraction of PAC embedded in the sludge flocs was fed to the anoxic compartment, promoting MP removal in this environment. AC may also reach the biological reactor in a different way. This is the case in schematic representation V in Table 1: PAC is used as a PT followed by a UF unit for its separation. The recirculation of the retained PAC back to the MBR, promotes its mixing with activated sludge and thus improves MP sorption and degradation (Lipp et al., 2012). Based on previous studies, it emerges that useful considerations can be found in (Streicher et al., 2016) who suggested that the long contact time in the activated sludge processes might enhance the PAC removal efficiency of many MPs compared to the short contact times in case of PT and that PAC addition in the anoxic

tank seems to be the best option. Finally, (Boehler et al., 2012) reported that similar removal of MPs can be achieved by adding 10-20 mg PAC/L in the case of a PT (DOM in the range 5-10 mg/L) and 30-40 mg/L of PAC if it is added in the biological tank.

6.1.5 Duration of the added PAC

The removal of an MP is strictly related to the working age of the AC: once it is added in the bioreactor, the whole surface is available for sorption and all the active sites are free (Figure 1B). After a period of operation, some sites are occupied by MPs and DOM and the removal may be lower than in the case of fresh AC. Once sorbed, the MP can be stable or subjected to biodegradation processes, leading to transformation products which could leave the carbon surface or remain sorbed on it (Baresel et al., 2019). As reported in section 3.2.3, doses of PAC added in the biological treatment varied between 0.004 g/L (Remy et al., 2012) and 20 g/L (Asif et al., 2020). Removal data provided in the studies are seldom correlated to the AC working age: only 8 studies provided removal as a function of time (Alvarino et al., 2017, 2016; Li et al., 2011; Löwenberg et al., 2014; Nguyen et al., 2014, 2013a; Serrano et al., 2011; Wei et al., 2016). In order to guarantee a good performance of the AC present in the treatment, (Alvarino et al., 2017) validated a dosage of 250 mg/L added every 35 days.

6.1.6 Sludge retention time

(Ng et al., 2013) evaluated the influence of SRT in hybrid MBRs (configurations I and II in Table 1, SRT=10 d, 30 d and > 100 d). At lower SRTs, a higher amount of fresh PAC is required to maintain a fairly constant AC concentration in the bioreactor. This would provide a higher adsorption of MPs and DOM and at the same time this practice would reduce the risk of membrane fouling. Higher SRTs promote the development of a diverse biomass species within the biological compartments and thus they would favour MP biodegradation processes. Specific investigations on the influence of SRT on the removal of MPs were not carried out in the reviewed studies: SRT ranged between 12 d (Echevarría et al., 2019) and 300 d (Nguyen et al., 2014) and no relevant removal differences were found.

6.1.7 Hydraulic retention time in PAC tank

According to kinetic studies, such as those by (Kovalova et al., 2013a; Mailler et al., 2016; Meinel et al., 2015), contact time influences the MP removal rate. They found that short HRT (30–60 min) may be enough to guarantee an efficient adsorption of most MPs (including atrazine, norfloxacin, ofloxacin and sulfamethoxazole). Larger molecules, such as erythromycin and roxithromycin require more than 1 h to achieve high removal. Moreover, adsorption is faster in the case of finer AC. In the reviewed studies, the tested HRT for the PAC tank as a PT varied between 0.5 h and 24 h and it allows the transfer of most of the MPs

from the liquid to the solid phase. According to (Lee et al., 2009), in submerged MBR, high HRT, low flux and intense mixing in the bioreactor are the best operational conditions to maintain the PAC in the bulk phase and reduce its deposition against the membrane. In fact, they found that PAC against the membrane reduces its sorption available surface thus its potential removal capacity. These findings refer to investigations carried out with deionised water, where biodegradation cannot occur for the investigated compound (E2). It is important to remark that the retention time of the PAC in the tank is another fundamental parameter, as remarked in section 4, but unfortunately it is not possible to correlate MP removal data to PAC retention time due to lack of data.

6.1.8 Dissolved organic matter

DOM is due to large organic molecules (biopolymers, humic substances and building blocks) and smaller molecules (low molecular weight organic acids and neutrals). Similar DOM concentrations (expressed as mg DOC/L) were found in the different compartments of the bioreactor as well as in a CAS effluent and in an MBR permeate, ranging between 5 mg/L and 18.4 mg/L (Altmann et al., 2014b; Fundneider et al., 2021a; Kovalova et al., 2013b; Meinel et al., 2015; Streicher et al., 2016). Based on Liquid Chromatography – Organic Carbon Detection (LC-OCD), it was found that different percentages of DOM constituents may occur (Altmann et al., 2014b; Filloux et al., 2012; Guillossou et al., 2020; Streicher et al., 2016; Zietzschmann et al., 2016, 2014) depending on the initial raw wastewater and the treatment. Interesting analyses of DOC in the wastewater under treatment were carried out in (Fundneider et al., 2021a, 2021b) also by size exclusion chromatography coupled with online DOC and UV_{254}, together with fractionation of the DOC and sorption potential of each fraction. They found that the non-adsorbable DOC in wastewater was around 20 %, in agreement with the results achieved by (Zietzschmann et al., 2014).

As mentioned above, DOM may affect MP removal as it can compete for available surface/sorption sites and, to a lesser extent, pore blockage, depending on its characteristics (average molecular weight and hydrophobicity) and AC porosity (De Ridder et al., 2011). This fact is clearly evident in (Dickenson and Drewes, 2010; Guillossou et al., 2020; Zietzschmann et al., 2016) who compared the removal curves of a selection of MPs at the same dosage of PAC ~~(20 mg/L)~~ in ultrapure water, drinking water and wastewater. According to the investigations by (Dickenson and Drewes, 2010), the observed removal was almost complete for all the compounds in the first case and in the range 50% to 75% in the presence of DOM.

Background DOM decreases adsorption capacities to a greater extent than pH, ionic strength,

and temperature. This occurs especially at low carbon doses where the competition for sorption sites is strong (Kovalova et al., 2013a). According to (Zietzschmann et al., 2014) the different fractions of DOM present a different adsorption behaviour: small molecules adsorb quickly and overall better, instead large molecules show slow and lower adsorption. The effect of small DOM molecule competition seems to affect particularly medium and low adsorbable MPs. In this context, (Zietzschmann et al., 2016) found that low molecular weight organics are the main competitors for the active sites in AC, and the estimation of their concentration can be useful in evaluating the required AC dose to reach a desired MP removal. On the other hand, (Guillossou et al., 2020) found that in the case of wastewater characterised by a modest fraction of low molecular weight organics, the competition in adsorption is due to biopolymers and hydrophobic molecules. Moreover, MPs may also interact with non-adsorbable DOM and thus remain in the liquid phase (Mailler et al., 2016).

Many authors suggest correlating MP removal to the PAC dose normalised to the respective DOC (that is the specific PAC dose, expressed in terms of mg PAC/mg DOC) (among them: Kovalova et al., 2013b; Streicher et al., 2016; Zietzschmann et al., 2016). This parameter makes it possible to estimate the required dose of a given PAC able to achieve the desired removal of the selected MP from the wastewater under treatment.

DOM adsorbed onto activated carbon is generally negatively charged at the pH of the wastewater and thus can decrease the adsorption of negatively charged MPs through repulsive electrostatic interactions (De Ridder et al., 2011) and increase the attraction of positively charged compounds (Mailler et al., 2015). At the same time, MPs may interact with DOM through Van der Waals bonds, as well as covalent and hydrogen bonds, resulting in a higher removal in MBR systems. This was found for bisphenol A which can interact with microbial by product-like and humic acid-like DOM in wastewater, and carbamazepine and ibuprofen with fulvic acid-like compounds (Hernandez-Ruiz et al., 2012). These complex phenomena are also affected by a high ionic strength in the liquid phase which can reduce the effect of electrostatic repulsion and attraction (De Ridder et al., 2011). Moreover, the DOM attached to the surface may be a barrier for those compounds whose removal is mainly due to adsorption on the activated sites, such as carbamazepine, diclofenac, diazinon and naproxen (Rattier et al., 2012). (Guillossou et al., 2020) showed that sufficiently long contact times allow a high removal of many MPs, despite an increase in DOM sorption on AC. This fact was ascribed to a slow diffusion of MPs through the adsorbed DOM on the PAC surface or to the formation of DOM-MPs complexes which are progressively adsorbed on the PAC surface. As highlighted above, proper HRTs can guarantee the transfer of MPs from the

liquid to the solid phase.

The interest toward DOM in the study of adsorption processes has increased in recent years being the adsorbed DOM (mg DOC/g GAC) the proposed assessment parameter of the performance of the GAC column instead of the commonly adopted EBV (Fundneider et al., 2021a).

6.1.9 Main factors affecting MP removal by GAC

In a GAC column it is crucial to adopt proper EBCT and filtration velocity v_f. EBCT is a key factor for the design of the GAC column, influencing the breakthrough curves of MPs. Generally, shorter EBCTs may lead to a lower adsorption of MPs. In this context, v_f and column height can be adjusted in order to guarantee a proper EBCT for removing the different MPs (Fundneider et al., 2021a). In the reviewed investigations, EBCT was between 7 and 50 min and the filtration velocity in the range 0.4–4.67 m/h (Baresel et al., 2019; Nguyen et al., 2013a, 2013b, 2012; Paredes et al., 2018)(Sbardella et al., 2018). Investigations were carried out at a lab scale with the only exception of (Baresel et al., 2019) who was at a pilot scale plant. A comparison of the adopted values of EBCT and v_f and those provided by the literature (Metcalf & Eddy, 2014) (510 min; 515 m/h as well as filter bed height in the range 24 m) shows that:

- EBCT in these investigations is generally higher (with the exception of (Nguyen et al., 2013b, 2012) where EBCT is around 7 min);
- v_f is always less than the minimum literature recommended value;
- as to the height, in lab scale investigations it was between 0.12 m and 0.42 m, in the pilot plant it was 1 m.

The adopted operational conditions (very slow filtration velocity and high EBCT) promoted the transfer of MPs from the liquid to the solid phase and counterbalanced the fact that the bed height was always less than the suggested one.

As to EBCT influence it is important to underline some main results. According to (Fundneider et al., 2021a) the smaller the grain size, the larger the specific surface area of the GAC and the shorter the EBCT to reach the equilibrium conditions for the MP mass transfer from the liquid phase to the solid phase. In their investigations, they correlated the MP removal capacity of the GAC column with the DOC sorbed on the GAC mass. They found that operating with EBCT between 6 and 24 min, the measured sorbed DOC on the GAC was higher for GAC columns operating with higher EBCT. With EBCT in the range 24–33 min, no differences were found. Moreover, they found that EBCT $\leq$ 20 min has a stronger

influence on the removal of well adsorbable MPs (among them benzotriazole, carbamazepine and ibersartan) than on the removal of poorly/moderately adsorbable compounds (such as primidone, and gabapentin). This leads to suppose that there is a value for EBCT after which the utilisation capacity of the GAC cannot be further improved. Moreover, they found that longer EBCTs have a positive effect on biological processes which take place within the grains of the GAC column. They reported that the EBCT increment promotes the substrate uptake by the biofilm developed on the grain surface in agreement with (Terry and Summers, 2018). They concluded that there is a minimum value of EBCT allowing MP removal by sorption and that an EBCT increment leads to an enhanced removal of MP and a better utilisation of the sorption capacity of the GAC column.

As to MP influent concentration, (Zietzschmann et al. 2016) found that, below the threshold of 50 mg/L, it did not impact the breakthrough curve of the investigated compound (benzotriazole, carbamazepine and primidone)which was instead impacted by the low molecular weight organics occurring in the wastewater fed to the GAC filter.

Finally, some attempts to investigate MP removal by Langmuir and Freundlich isotherm adsorption curves (Nguyen et al., 2013b; Paredes et al., 2018) pointed out that there is no clear evidence of direct correlations between isotherm parameters and any of the governing parameters such as Log D_{ow}, number of hydrogen bond donor/acceptor groups, dipole moment or aromaticity ratio of the compounds (Nguyen et al., 2013b).

6.1.10 Behaviour of the GAC filter over time

GAC filter removal capacity decreases over time due to the granules increasing saturation by MPs and DOM. MP and DOM loads (mass/time) are crucial parameters affecting the expected operation time. Many authors investigated the GAC filter saturation process through the so called breakthrough profiles which report the ratio between MP effluent concentration c_{eff} and its influent concentration c_{inf} vs EBV (Baresel et al., 2019)(Nguyen et al., 2012)(Kovalova et al., 2013a; Nguyen et al., 2013b; Paredes et al., 2018). Rapid small-scale column tests (RSSCTs) represent a suitable option to determine breakthrough curves faster than pilot GAC columns. RSSCTs are a scaled-down version (by simple design equations) of pilot GAC beds allowing sorption studies to minimise removal via biodegradation (Crittenden et al., 1991; Zhiteneva et al., 2020).

Once adsorbed on AC, as discussed in (Baresel et al., 2019; Fundneider et al., 2021b), some MPs (among them oxazepam, carbamazepine and diclofenac) may undergo biodegradation, leading to transformation products which may leave the AC surface, thus contributing to AC filter bioregeneration. They noted that for oxazepam it was clearly evident that after 25,000

EBV there was a sharp increment in the ratio c_{eff}/c_{inf}, followed by a consistent decrement due to GAC bioregeneration which allows new molecules of oxazepam to be sorbed. This fact is discussed in (Benstoem et al., 2017) who found a good removal of adsorbable MPs when DOM equilibrium in the GAC column is reached. Moreover, it was also observed (Sbardella et al., 2018) that when the carbon is completely saturated (at long operating times), some MPs (for instance azithromycin) exhibit a modest but constant removal which could be ascribed to the biodegradation process still occurring within the BAC.

Figure 7 reports the removal efficiencies for the reviewed compounds as a function of EBV. It emerges that for some compounds, good removal occurs after a long operation time (really high EBV) for the reasons just discussed, but also for a low influent MP and DOM load (Paredes et al., 2018)(Sbardella et al., 2018).

Investigations on the GAC filter lifespan are in any case necessary in order to plan periodical regeneration or replacement of the exhausted AC, as recommended (Nguyen et al., 2013a, 2013b, 2012).

Very recent studies remarked that the parameter EBV does not take into consideration the fluctuations in influent in terms of MP concentration and load which are fundamental for the GAC column lifetime and the breakthrough point. In addition, a variation in the influent flow rate results in an EBCT variation. For these reasons, (Fundneider et al., 2021a) propose the adsorbed DOC (mg DOC/g GAC) as the assessment parameter of GAC column performance as it is independent of the influent fluctuations of concentrations and flow rate and (Zietzschmann et al., 2016) propose the low molecular weight organics per mass of GAC (mg C/g GAC) and the UV_{254} per mass of GAC. According to (Fundneider et al., 2021a) recommendations and guidelines will be available in the near future for the efficient design and operation of GAC columns acting as a PT in WWTP by DWA, the German Association for Water, Wastewater and Waste.

6.1.11 Other parameters influencing MP removal in MBR coupled with AC

Temperature. It is well known that an increment in temperature leads to a decrement in sorption of an MP (Nam et al., 2014), whereas it enhances its biodegradation (Alvarino et al., 2018).

Addition of the coagulant $FeCl_3$. An addition of the coagulant (4–15 mg/L) to the secondary effluent already mixed with PAC may lead to an improvement in membrane permeability and to control the TMP increase (Löwenberg et al., 2014). It may also favour the separation of the PAC (Margot et al., 2013). In the patented fluidised PAC bed (CarboPlus©), acting as a PT following an attached biomass system, $FeCl_3$ was added (2.5 mg/L) to stabilise the PAC

bed and prevent PAC leakage (Mailler et al., 2015). They found a slight enhancement in the removal of carbamazepine, beta-blockers and diclofenac (5% to 15%), probably due to coagulation of the colloidal fraction, a lower removal for sulfamethoxazole (-30%) and no change for lorazepam and bezafibrate.

Redox conditions. Once PAC is added, a biofilm may develop on its surface, with aerobic and anoxic zones, thus creating a gradient in redox potential. Over time, the anoxic zone develops and the community structure changes, favouring the species diversity in the anoxic zone (Zhang and Zhao, 2014).

In particular, it was found that PAC addition promotes the development of nitrifiers which favour the degradation of some MPS, mainly hormones and ibuprofen (Alvarino et al., 2018). (Alvarino et al., 2016) found that denitrification might occur to some extent also during the aerobic phase. This was due to the growth of a biofilm on the added PAC able to adsorb nitrate ions. This implies the coexistence of anoxic and aerobic zones and thus the development of MP degradation processes occurring under different redox conditions.

Type of membranes. The size of the membranes (MF and UF), equipped in MBRs, slightly influences the removals of MPs. It was found that for diclofenac the removal was higher in the case of UF (Alvarino et al., 2017). This fact can be ascribed not to MP size exclusion, but to its sorption on smaller particles retained by the cake layer grown against the membrane.

6.2 Influence of the AC on the MBR operation

Most of the investigations on MBR coupled with AC in recent years have dealt with the removal of macropollutants, membrane fouling, analysis of the operational conditions and factors influencing and enhancing micropollutant removal. This section briefly discusses the main issues related to macropollutant removal, membrane fouling mitigation and sludge property changes.

6.2.1 Effluent quality

The presence of AC favours the development of the biomass leading to a slightly higher concentration of the biomass. This could be ascribed to the sorption of organic matter onto the AC surface in the reactor which is then available to microorganisms for their anabolic activities (Cho et al., 2011; Guo et al., 2008; Johir et al., 2013). As to organic matter (COD, BOD_5, DOC) and suspended solids, it was found that the presence of AC may slightly improve their already high (> 95%) removal in MBR (Guo et al., 2008)(Johir et al., 2013). A DOC removal of 81% was observed in the MBR investigated by (Gao et al., 2016) and a very low removal of aromatic compounds with unsaturated bonds which led to a 34% reduction in UV_{254}. The addition of 1 g/L of PAC in the bioreactor not only incremented the DOC

removal up to 91%, but strongly increased the removal of UV_{254} up to 83%. This was explained with the fact that organic compounds, both recalcitrant and easily degradable ones, are directly adsorbed on PAC, then they gather around the bacteria favouring the biodegradation of the recalcitrant compounds. Decrease in UV_{254} is therefore related to the adsorption of aromatic rings, both from MPs and DOM constituents of wastewater (Altmann et al., 2014a; Streicher et al., 2016). As to nitrogen removal, studies remarked that PAC addition may lead to an increment of around 10% (Echevarría et al., 2019)(Serrano et al., 2011) due to the formation and growth of a biofilm layer on the adsorbent surface that creates anoxic zones enabling denitrification, as well as an enhancement of nitrifiers (Alvarino et al., 2018). As to P, the observed removal efficiencies in MBR are low to moderate and do not significantly change with the presence of AC (Johir et al., 2013). It was found that the addition of 20 g/L of PAC may promote the development and growth of polyphosphate-accumulating-organisms (PAOs) which led to a 10% increment in the removal of total phosphorus from the wastewater (Asif et al., 2020). To sum up, the different removals achieved may be ascribed to a change in the composition of the mixed liquor (Pan et al., 2016).

6.2.2 Mitigation of the membrane fouling

Most of the studies have dealt and are still dealing with the mitigation effects on the membrane fouling, one of the most critical problems to face and manage with membrane technologies (Iorhemen et al., 2017, Zhang et al., 2019). According to the nature of foulants, fouling can be divided into: *bio-fouling* related to the attached microorganisms on the membrane surface; *organic fouling* due to polysaccharides, proteins, colloidal and humic substances, and bio-polymers and *inorganic fouling* caused by salts, scalants, metal oxides and other inorganic substances (Gkotsis and Zouboulis, 2020). Deposition and attachment of foulants on the membrane surface lead to an increment in hydraulic resistance. As a result, the transmembrane pressure (TMP) increases and the flux through the membrane declines (Woo et al., 2016). Curves of TMP *versus* operation time shows a first stage in which the membrane does not require cleaning and TMP slightly increases, then in the second stage a sudden increase occurs. (Jamal Khan et al., 2012; Lin et al., 2011) found that the addition of 0.751 g/L of PAC approximately doubles the duration of the first stage, whereas (Zhang et al., 2019) suggest 2 g/L as the optimum dosage of PAC as a mitigation strategy of membrane fouling control. In the field of the urban wastewater treatment, the principal fouling which may occur is organic fouling. In order to avoid fouling, it is necessary to retain foulants with adequate pretreatments that are able to reduce their content in the water under treatment.

As described in section 4, once AC is added in the biological tank, microorganisms and DOM are retained on its surface: their lower concentrations in the liquid phase reduce the membrane organic fouling and biofouling (Gao et al., 2016). Another positive effect of AC addition in the MBR is that it leads to an enhancement of the sludge floc strength (as will be discussed later on). As a consequence, the strong floc structure with incorporated AC will release fewer foulants (soluble COD, proteins and polysaccharides, Ca^{2+}, Mg^{2+}) and thus will reduce the formation of the gel-layer on the membrane (Remy et al., 2010) (Johir et al., 2011). The velocity with which the membrane fouls depends on the TOC concentration in the water under treatment; the *flux*, that is the specific flow rate through the membrane, expressed in L/m^2 h, and the added AC size (Ng et al., 2013). They found that membrane fouling prevention can be optimised by using: *(i)* fine rather than coarse PAC as it better reduces the TOC in the bulk phase; and (*ii)* relatively short SRTs (around 10 days), as they favour organic matter adsorption. At the same time, in order to reduce smaller AC particle deposition, flux must be carefully set also on the basis of the aeration system used to detach foulants.

6.2.3 Changes in sludge properties after the PAC addition

PAC addition in the bioreactor leads to an enlargement of the floc size: the average sludge particle size was found around 90 □m in an MBR (70% in the range 10–100 □m) and 128 □m in an MBR + PAC (37% in the same range) (Pan et al., 2016). The sludge flocs enlarge because added PAC neutralises their negative surface charge, causing them to agglomerate (Zhang et al., 2017). The larger flocs increase their strength and are able to withstand greater impacts during aeration (Pan et al., 2016). They lead to a low content of SMP and/or EPS contents in the mixed liquor (Pan et al., 2016) (Zhang and Zhao, 2014) (Remy et al., 2010).

PAC addition also leads to a change in the chemical composition of the sludge floc which results in a different sorption potential (Yang et al., 2012; Yu et al., 2014). It was also found that the PAC-embedded sludge floc exhibited a higher sorption capacity of recalcitrant aromatic compounds, resulting in a reduction in UV_{254} (Gao et al., 2016; Pan et al., 2016).

The sludge with incorporated PAC has better settling characteristics since less compressible flocs are formed. In this context, (Johir et al., 2013; Pan et al., 2016) found that the sludge volume index (SVI) for MBR sludge was around 90–110 mL/g and in the case of MBR+AC, it was reduced to 50–70 mL/g. The presence of PAC within a sludge floc leads to a cake layer against the more porous membrane than in the absence of PAC: a higher volume percentage of particles was found in the range 300–700 mm in the case of MBR+PAC than in MBR operating with the same MLVSS (Jamal Khan et al., 2012), (Lin et al., 2011).

7 Conclusive considerations and need for further research

The current overview shows the effective contribution of AC in (advanced) biological wastewater treatment in enhancing the removal of many MPs and at the same time the improvement of MBR performance (increment in the removal of the discussed macropollutants, mitigation in membrane fouling and improvement in sludge characteristics). Collected results are strictly related to MP nature, AC characteristics and the presence of DOM in wastewater and the complex interactions among these three actors define the MP removal efficiencies. Although there is not a well-defined PAC dose to add in the MBR to reach a minimum removal for all the MPs, with a PAC of 0.1 g/L, 80% of removal was achieved for most of the tested compounds. MP removal efficiencies show a greater variability when PAC is in the PT in comparison to when it is added in the bioreactor. Moreover, it emerges that the effect of the presence of DOM is more evident in the case of PAC as a PT. MP removal efficiency in the GAC unit working as a PT is highly dependent on MBR performance. For compounds with a moderate removal efficiency in MBR (such as ketoprofene), GAC can exhibit fairly constant removal until its saturation. It was also found that GAC may adapt to the MP loading fluctuations in the column influent and guarantee fairly constant effluent quality (such as for metronidazole). If GAC becomes BAC, biodegradable compounds retained on its surface may still maintain a good removal efficiency at long operation times due to biodegradation processes in biofilm. In the case of MPs whose main removal mechanism is adsorption, GAC column bioregeneration is essential in order to allow a high and continuous MP removal.

A loss in AC *potential* adsorption capacity occurs due to its progressive saturation and its removal from the system through excess sludge withdrawal or the retentate from the membrane PT unit. PAC addition (replenishment) is thus necessary to maintain its desired concentration in the tank.

AC influences the MBR operation mainly by changing the composition of the mixed liquor. The concentration of organic compounds in the liquid phase of the biological tank is reduced by the attachment of DOM onto the AC surface. The presence of AC in the floc increases its strength and improves its settling characteristics. The cake layer against the membrane becomes more porous than when AC is absent. AC added in the bioreactor prolongs MBR operation by mitigating membrane fouling.

Recent studies proposed to analyse MP removal as a function of the DOC adsorbed on the AC (mg DOC/mg AC) as it better reflects the saturation level of the AC present in the studied system over time.

Further studies are necessary to better investigate the interactions between DOM and the different MPs with regard to the characteristics of DOM (biopolymers, hydrophobic molecules) and the role played by inorganic ions (for instance cations). Moreover, the contributions due to adsorption and biodegradation to MP removal may be identified under controlled conditions, by comparing the performance of a biologically inactivated GAC with a BAC. Values of biological constant rate k_{biol} when AC is added in MBR could be useful to predict the potential enhancement of the biodegradation of selected MPs as well as K_d values showing MP sorption potential when PAC is added in MBR or AC unit acting as a PT. Their knowledge will make it possible to understand which removal pathway mostly contributes to the removal of a specific compound, despite the fact a multiparametric equation is not available to predict the behaviour of a compound in such a complex system.

Analysis of the performance of specific configurations should also include the monitoring of UV_{254}. This parameter quickly provides an indirect measure of the occurrence of many low molecular weight organics. For this reason, it was considered a surrogate for MP occurrence in influent and effluent, but it could also become a reliable surrogate of low molecular weight organics belonging to the DOM.

Finally, investigations on real wastewater are necessary to better understand the removal mechanisms with regard to compounds of great concern or which could represent a group of compounds characterised by a similar behaviour in hybrid MBRs like those coupled with AC. Investigations on synthetic wastewater represent a useful step in the research, but they should be validated with real wastewater.

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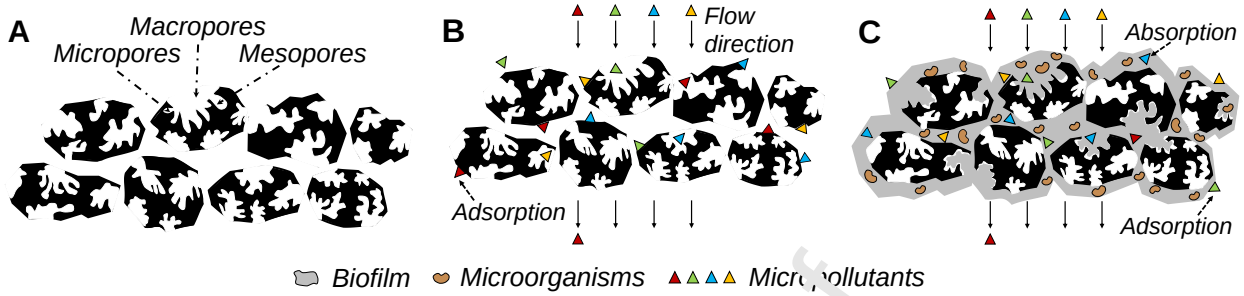


Figure 1. Schematic representation of (A) the structure of activated carbon; (B) adsorption of micropollutants on the surface of the AC; (C) BAC, with micropollutants absorbed and adsorbed on its surface.

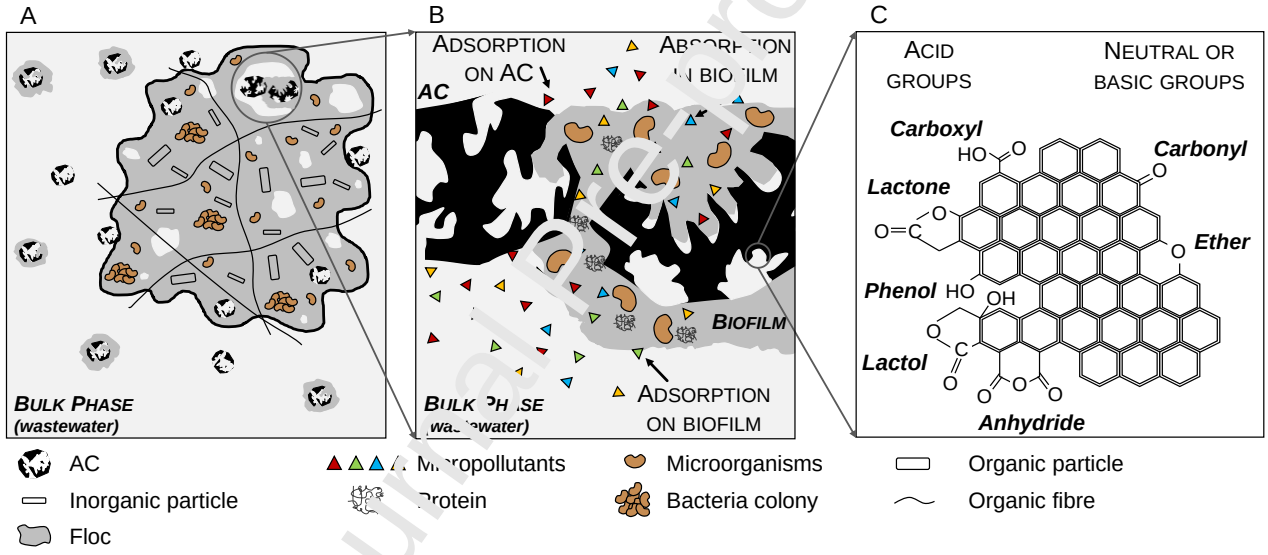
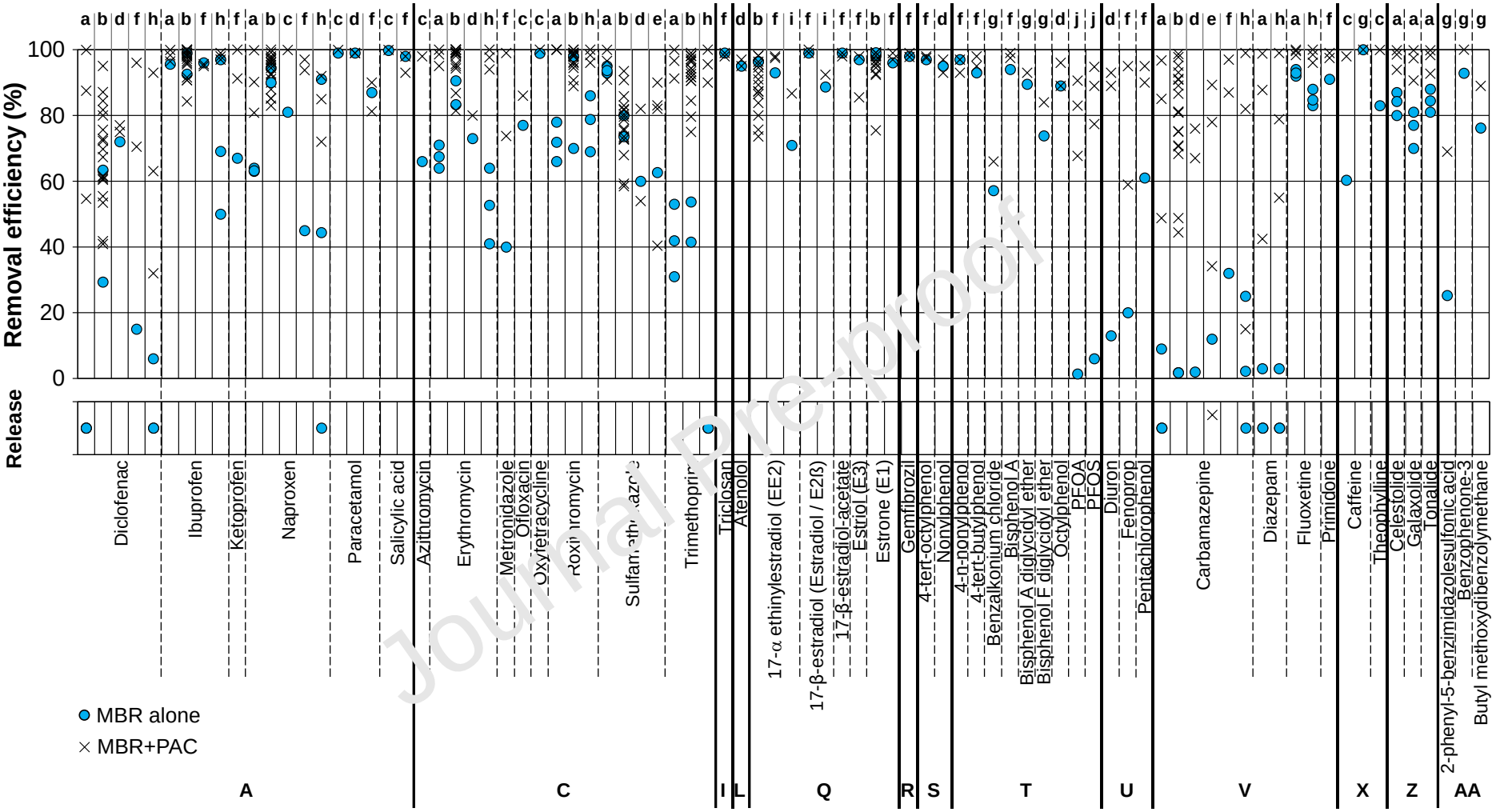
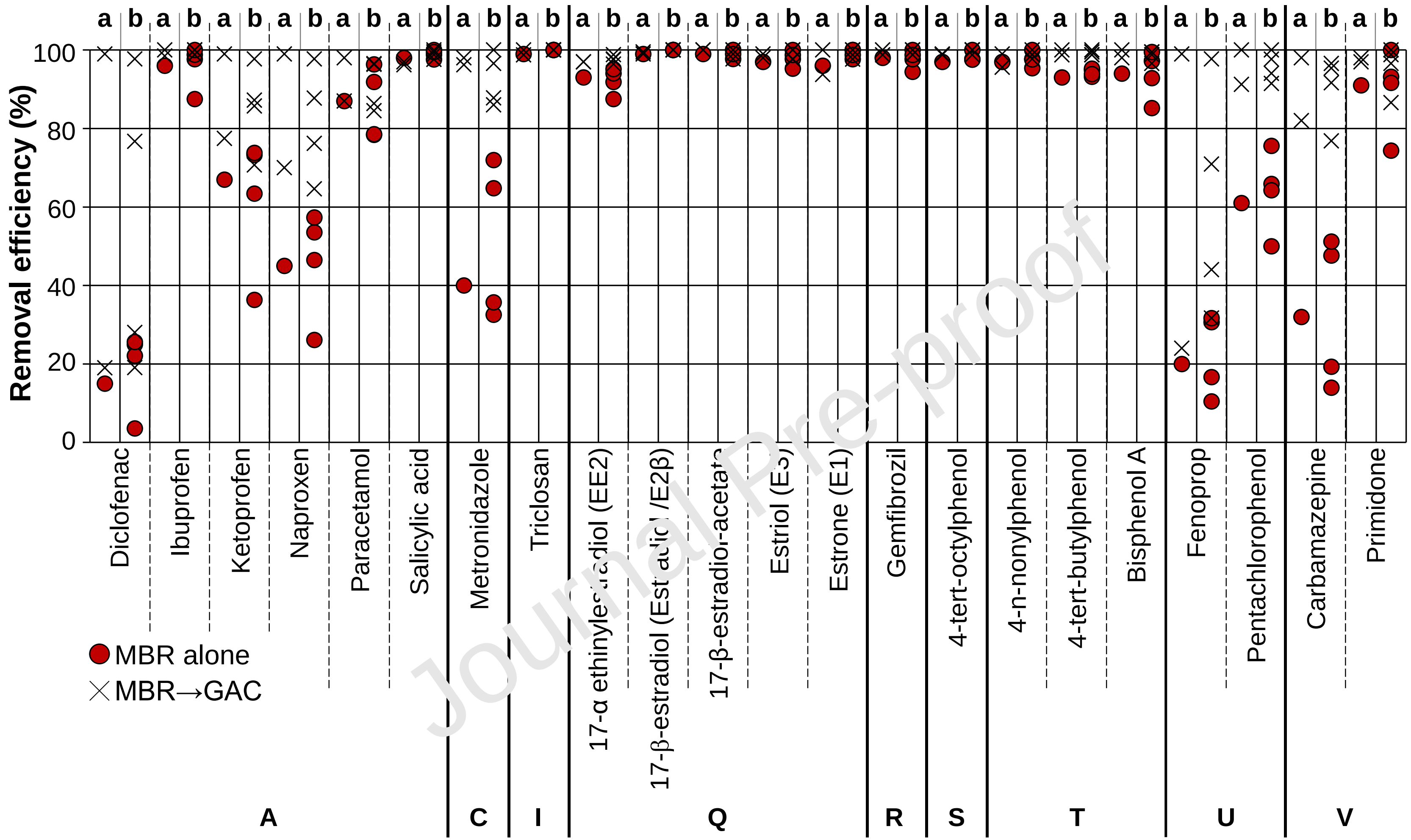


Figure 2. Schematic representation of a sludge floc in the bioreactor in the presence of AC (A); MP removal mechanisms in an AC particle incorporated in the sludge floc (B); main functional groups on the surface of AC (C).



a Alvarino et al. 2016; **b** Alvarino et al. 2017; **c** Asif et al. 2020; **d** Echevarría et al. 2019; **e** Li et al. 2011; **f** Nguyen et al. 2013a; **g** Remy et al. 2012; **h** Serrano et al. 2011; **i** Yang et al. 2012; **j** Yu et al. 2014

Figure 3. Comparison among removal efficiencies achieved in MBR alone and MBR coupled with PAC.



a Nguyen et al. 2013a; **b** Nguyen et al. 2013b

Figure 4. Comparison among removal efficiencies achieved in MBR alone and MBR coupled with GAC.

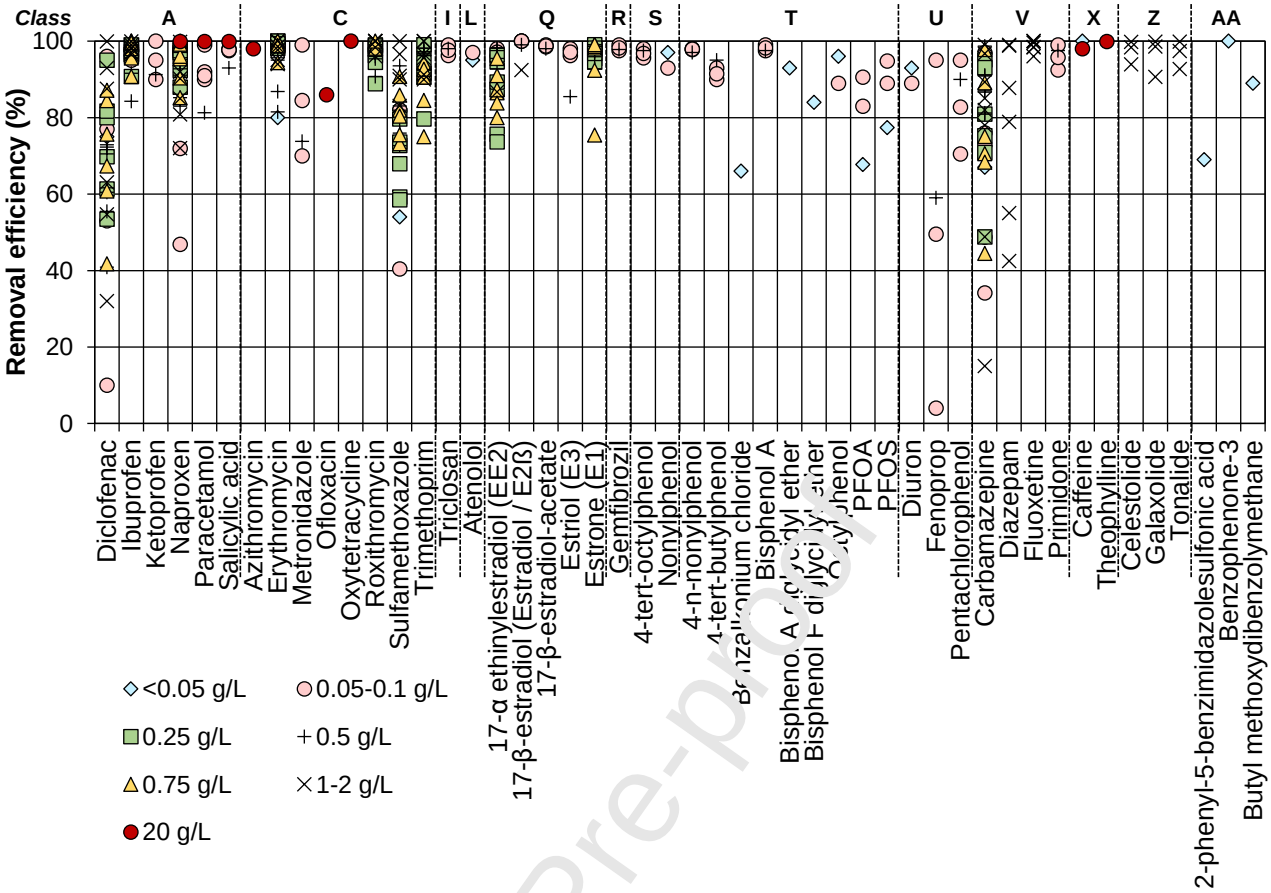


Figure 5. Removal efficiencies for the compounds investigated in MBR+PAC with a submerged or side stream membrane unit. Data from: (Alvarino et al., 2017, 2016; Asif et al., 2020; Echevarría et al., 2019; Li et al., 2011; Nguyen et al., 2013a; Remy et al., 2012; Serrano et al., 2011; Yang et al., 2012; Yu et al., 2014)

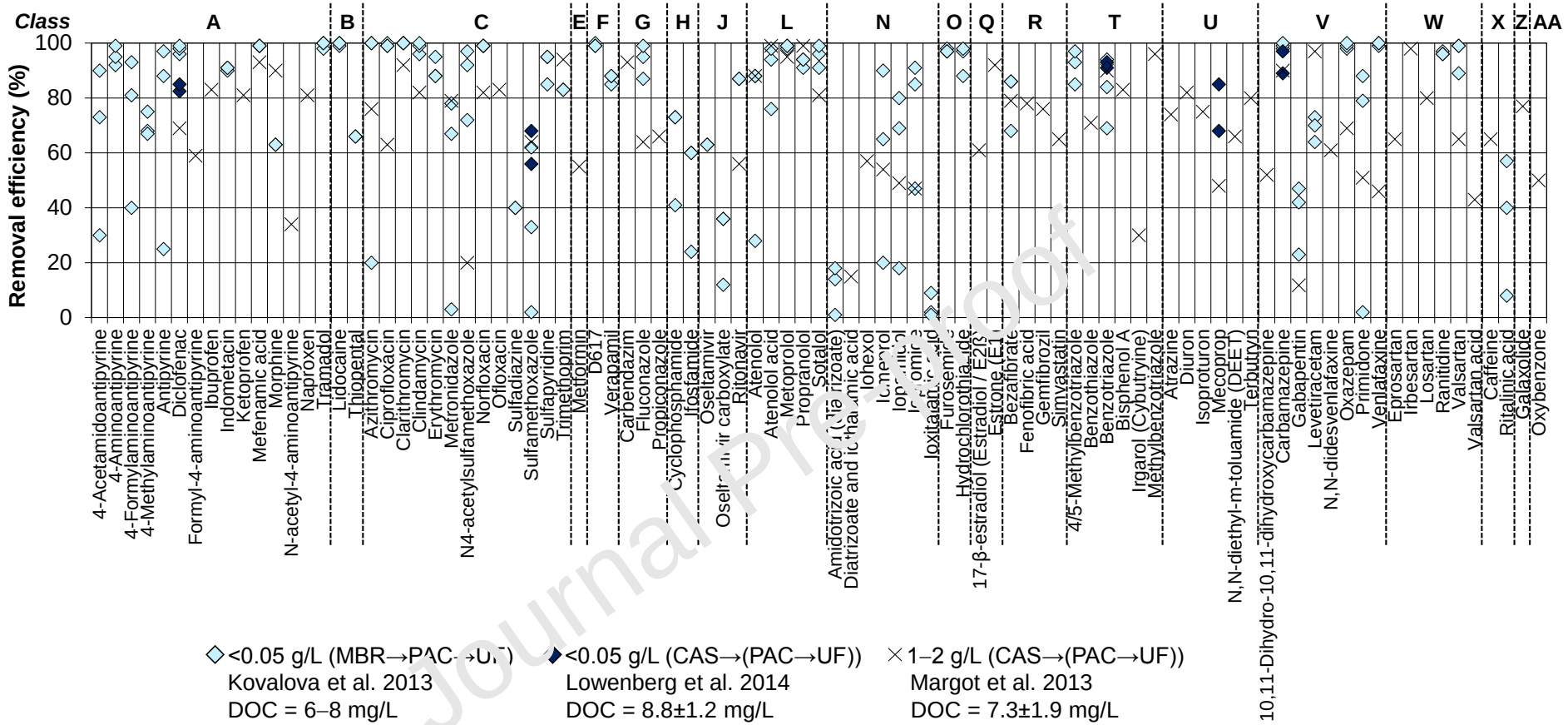


Figure 6. Removal efficiencies of the compounds included in the reviewed studies referring only to the PAC polishing treatment, following a CAS or an MBR. DOC concentrations refer to the secondary effluent fed to the PAC unit. Data from: (Kovalova et al., 2013b; Löwenberg et al., 2014; Margot et al., 2013).

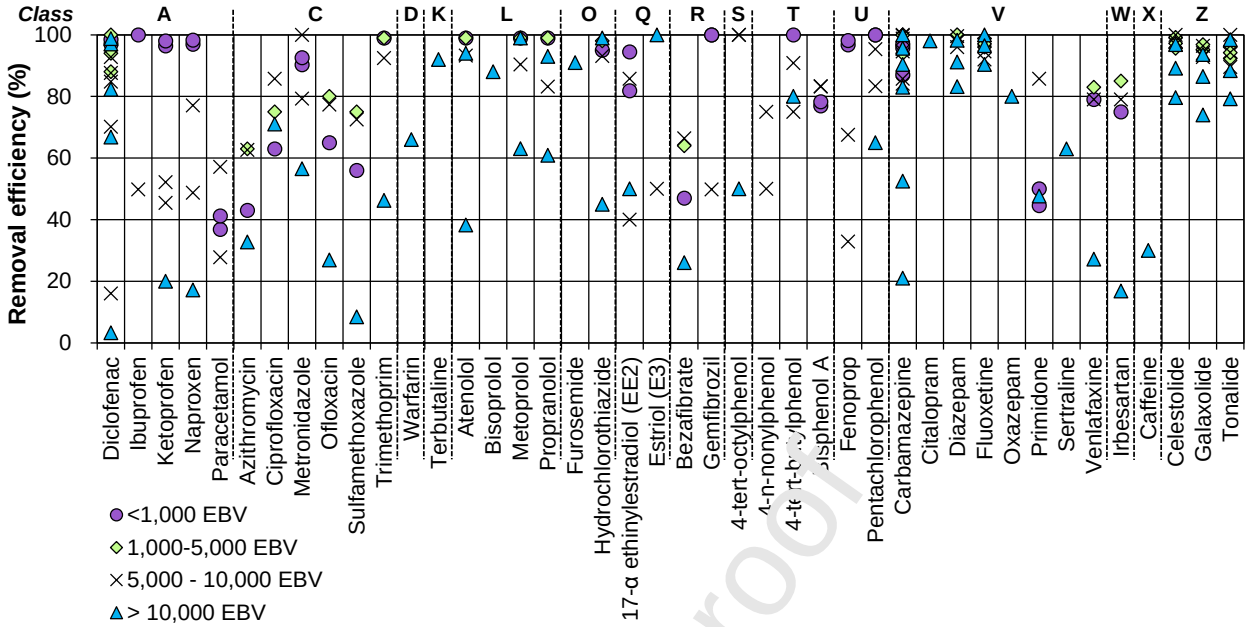


Figure 7. Removal efficiencies obtained in the GAC unit acting as a PT for the compounds under review at different empty bed volumes. Data from: (Baresel et al., 2019; Nguyen et al., 2013b, 2012; Paredes et al., 2018; Sbardella et al., 2018).

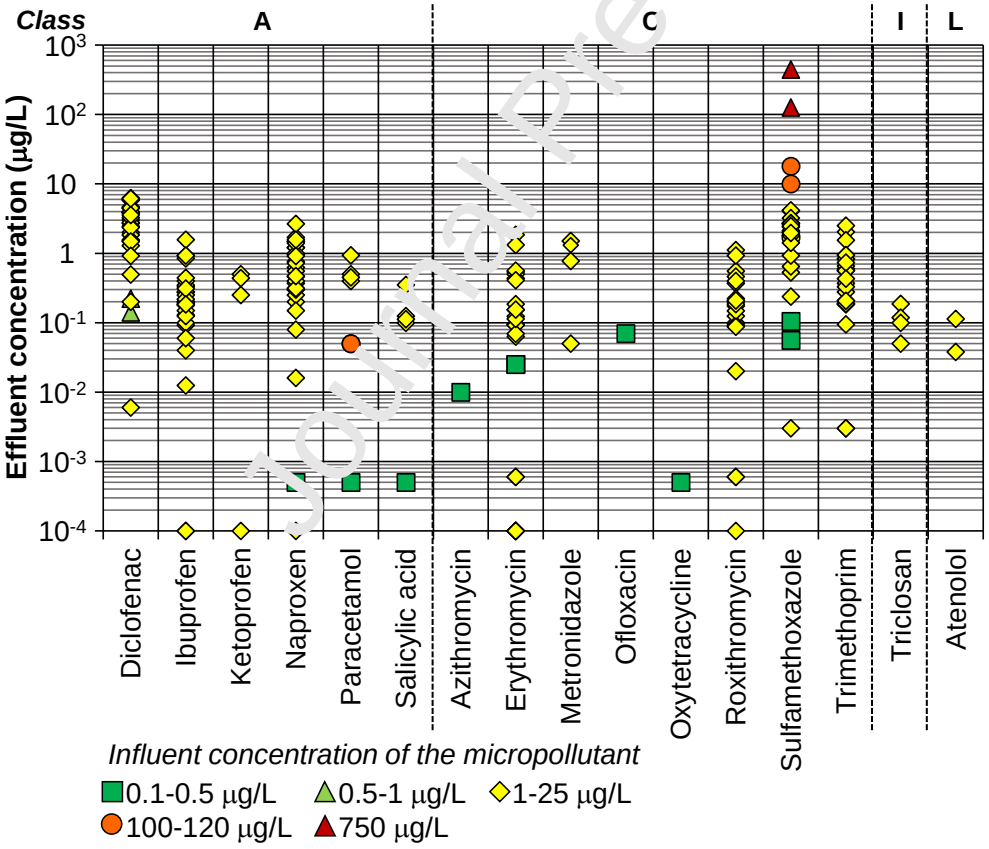


Figure 8. Concentrations of micropollutants in the effluent of MBR+PAC for some classes of micropollutants. Data are provided with respect to the micropollutants concentration in the corresponding influent. Data from: (Alvarino et al., 2017, 2016; Asif et al., 2020; Echevarría et al., 2019; Li et al., 2011; Nguyen et al., 2013a; Serrano et al., 2011; Yang et al., 2012)

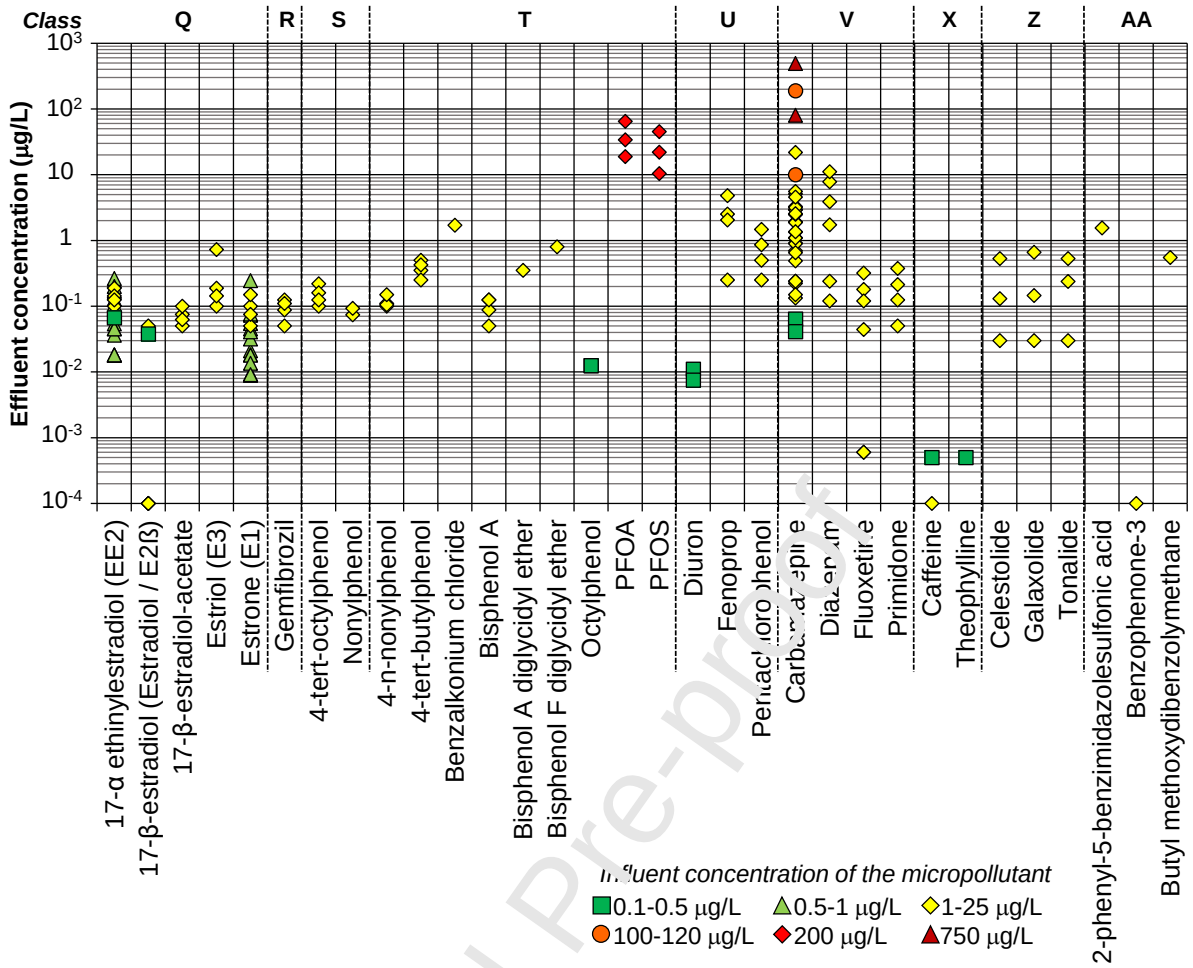
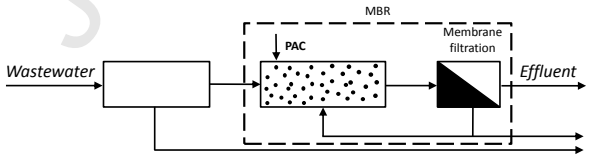
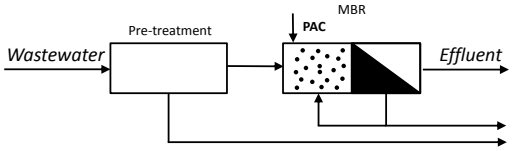
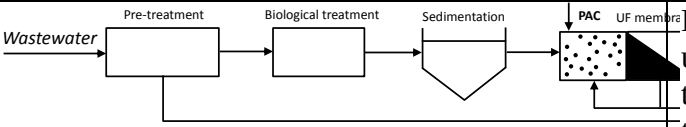
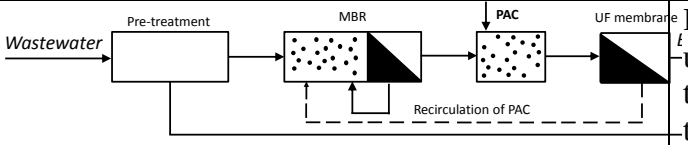


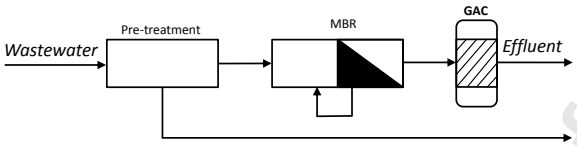
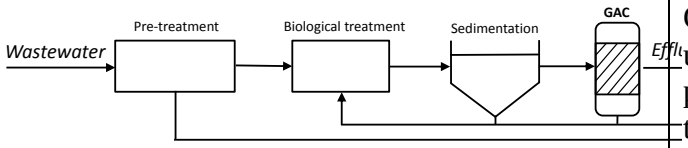
Figure 9. Concentration in the effluent of MBR+PAC for micropollutants belonging to the other classes included in the review. Data from: (Alvarino et al., 2017, 2016; Asif et al., 2020; Echevarría et al., 2019; Li et al., 2011; Nguyen et al., 2013a; Remy et al., 2012; Serrano et al., 2011; Yu et al., 2014)

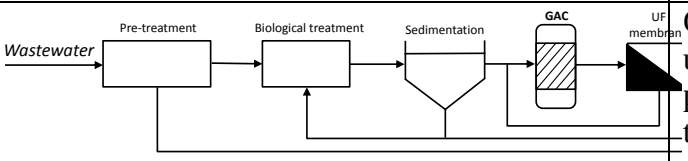
Table 1 Configurations of biological treatment coupled with AC considered in the review together with the corresponding references

Configuration		**Comments**	**References**
I Side stream **(MBR+PAC)**		PAC is added directly in the bioreactor. The membrane unit is in a separate tank. The sludge recycled into the bioreacto	Alvarino et al., 2016; Asif et al., 2020; Echevarría et al., 2019; Remy et al., 2012; Serrano et al., 2011, Wei et al., 2016;

		r contains an amount of (embedded) PAC. A fraction is lost with the excess sludge.	
II Submerged **(MBR+PAC)**		PAC is added directly in the bioreactor. The membrane unit is in the same reactor. The sludge recycled into the bioreactor contains an amount of (embedded) PAC. A fraction is lost with the excess sludge.	Alvarino et al., 2017; Li et al., 2011; Nguyen 2013a; Nguyen et al., 2014; Yang et al., 2010; Yang et al., 2012; Yu et al., 2014
III (PT) **CAS→(PAC+ UF)**		PAC is used in the post treatment. The CAS effluent is sent to the PAC and a UF	Löwenberg et al., 2014, Margot et al., 2013

		membrane unit retains the powder. A small amount is recycled. In Margot et al., 2013, 5% of the influent is treated in an MBBR and then mixed with the CAS effluent.	
IV (PT) **MBR→PAC→ UF**		PAC is used in the post treatment. The permeate is sent to the PAC and a UF membrane unit retains the powder. In the MBR there is no PAC.	Kovalova et al., 2013b
V (PT) **MBR→PAC→ UF** & recirculation		PAC is used in the post treatment. The permeate is sent to the PAC and a UF membrane unit	Lipp et al., 2012

		retains the AC powder and is completely recycled in the bioreactor.	
VI (PT) **MBR→GAC**		GAC is used as a post treatment. The permeate is sent into the GAC column and then directly discharged. In two studies (those with the asterisk in the adjacent column) there is an ozonation step between MBR and GAC.	Baresel et al., 2019; Itzel et al., 2018*; Langenhoff et al., 2013; Nguyen et al., 2012; Nguyen 2013a; Nguyen et al., 2013b; Paredes et al., 2018; Paulus et al., 2019*
VII (PT) **CAS→GAC**		GAC is used as a post treatment. The CAS effluent is sent into the GAC column	Grover et al., 2011

		and then directly discharged.	
VIII **CAS→GAC→ UF**		GAC is used as a post treatment. The CAS effluent is sent into the GAC column, then filtered (by UF membrane) and then discharged.	Sbardella et al., 2018

* An ozonation step is present between MBR and GAC column.

Table 2. Compounds included in the review grouped according to their class. In brackets, the number of compounds for each class considered in this study.

Class	Class Symbol	Compound
Analgesics/Anti-inflammatories (**18**)	**A**	4-acetamidoantipyrine; 4-aminoantipyrine; 4-formylaminoantipyrine; 4-methylaminoantipyrine; antipyrine/phenazone; diclofenac; formyl-4-aminoantipyrine; ibuprofen; indometacin; ketoprofen; mefenamic acid; morphine; n-acetyl-4-aminoantipyrine; naproxen; paracetamol/acetaminophen; salicylic acid; tramadol; *meclofenamic acid**
Anaesthetics (**2**)	**B**	Lidocaine; thiopental
Antibacterials (**29**)	**C**	Amoxicillin; ampicillin; azithromycin; cefalexin; ciprofloxacin; clarithromycin; clindamycin; erythromycin; flumequine; lincomycin; metronidazole; N4-acetylsulfamethoxazole; norfloxacin; ofloxacin; oxolinic acid; oxytetracycline; rifaximin; roxithromycin; sulfadiazine; sulfamerazine; sulfamethoxazole; sulfamethoxypyridazine; sulfamoxole; sulfapyridine; sulfathiazole; sulfisoxazole; trimethoprim; *doxycycline**; *tetracycline**
Anticoagulants (**1**)	**D**	Warfarin
Antidiabetics (**1**)	**E**	Metformin

Anti-hypertensives (**3**)	**F**	D617; verapamil; *enalapril**
Antimycotics (**4**)	**G**	Carbendazim; fluconazole; propiconazole; *ketoconazole**
Antineoplastics (**5**)	**H**	Cyclophosphamide; flutamide; hydroxytamoxifen; ifosfamide; tamoxifen
Antiseptics (**1**)	**I**	Triclosan
Antiviral (**3**)	**J**	Oseltamivir; oseltamivir carboxylate; ritonavir
Beta-agonists (**1**)	**K**	Terbutaline
Beta-blockers (**6**)	**L**	Atenolol; atenolol acid; bisoprolol; metoprolol; propranolol; sotalol
Calcium channel blockers (**1**)	**M**	Amlodipine
Contrast media (**7**)	**N**	Amidotrizoic acid (diatrizoate); diatrizoate and iothalamic acid; iohexol; iomeprol; iopamidol; iopromide; ioxitalamic acid
Diuretics (**2**)	**O**	Furosemide; hydrochlorothiazide
Gastrointestinal disorder drugs (**1**)	**P**	Mebeverine
Hormones (**14**)	**Q**	17α-ethinylestradiol (EE2); 17β-estradiol (Estradiol E2); 17β-estradiol-acetate; boldenone; boldione; cyproterone acetate; dihydrotestosterone; estriol (E3); estrone (E1); etiocholanolone; nandrolone; testosterone; *norethindrone**; *progesterone**
Lipid regulators (**5**)	**R**	Bezafibrate; fenofibric acid; gemfibrozil; simvastatin; *clofibric acid**
Non ionic surfactants (**2**)	**S**	4-tert-octylphenol; nonylphenol
Others (**15**)	**T**	4(5)-methylbenzotriazole; 4-n-nonylphenol; 4-tert-butylphenol; 5-methylbenzotriazole; benzalkonium chloride; benzothiazole; benzotriazole; bisphenol A; bisphenol A diglycidyl ether; bisphenol F diglycidyl ether; irgarol (cybutryne); methylbenzotriazole; octylphenol; perfluorooctanoic acid (PFOA); perfluorooctanesulfonic acid (PFOS); *tris(2-carboxyethyl)phosphine (TCEP)*; tris(1,3-dichloroisopropyl)phosphate (TDCPP)**
Pesticides (**8**)	**U**	Atrazine; diuron; fenoprop; isoproturon; mecoprop; N,N-diethyl-meta-toluamide (DEET); pentachlorophenol; terbutryn
Psychiatric drugs (**16**)	**V**	10,11-Dihydro-10,11-dihydroxycarbamazepine; carbamazepine; citalopram; diazepam; fluoxetine; gabapentin; levetiracetam; N,N-didesvenlafaxine; oxazepam; primidone; risperidone; sertraline; venlafaxine; *amitriptyline**; *dilantin**; *thioridazine**
Receptor antagonists (**7**)	**W**	Eprosartan; irbesartan; losartan; ramipril; ranitidine; valsartan; valsartan acid

Stimulants (**3**)	**X**	Caffeine; ritalinic acid; theophylline
Sweeteners (**1**)	**Y**	Aspartame
Synthetic musks (**3**)	**Z**	Celestolide; galaxolide; tonalide
UV filters (**4**)	**AA**	2-phenyl-5-benzimidazolesulfonic acid; benzophenone-3; butyl methoxydibenzoylmethane; oxybenzone
Veterinary drugs (**12**)	**BB**	Enrofloxacin; marbofloxacin; sarafloxacin; sulfachloropyridazine; sulfaclozine; sulfadimethoxine; sulfadimidine; sulfadoxine; sulfamonomethoxine; trenbolone; tylosin; *monensin**
*Anti-histamines **(1)***		*Diphenhydramine**
*Urological drug **(1)***		*Finasteride**

* Compounds investigated and never detected.

** For these classes a symbol is not set as they are not included in the graphs.

Table 3 Main characteristics of the activated carbon used in the reviewed studies

Type	**PAC**	**GAC**
BET specific surface area (m^2/g)	328 to 1,262	895 to 1,250
Particle size (µm)	15 to 40*	1,000 to 4,750
Pore volume (cm^3/g)	0.228 to 0.88	0.043
Pore diameter (nm)	2.6 to 3.13	3 to > 100
Iodine number (mg/g)	650 to 1,250	920 to > 1,200
Bulk density (g/cm^3)	0.25 to 0.42	0.42 to 0.50
pH_{pzc}	7 to 11	
Ash content (%)	6 to 14	3

* (in 2 cases up to)

Highlights

Micropollutants removal by MBR coupled with activated carbon is reviewed
Activated carbon in the bioreactor enhances the removal of most compounds
Low molecular weight organics are a strong competitor in sorption process
At a dose of 0.1 g PAC/L the removal efficiency of many compounds is around 80 %.
Biologically activated carbon column promotes the degradation of MPs.