Stockholm University
Analytical and Toxicological Chemistry
Environmental Science and Analytical Chemistry

ivl

Powdered activated carbon (PAC) addition in membrane bioreactor (MBR) for increased removal of organic pollutants in municipal wastewater

15 Credits
Advanced Level Undergraduate Thesis
in Analytical Chemistry

Sultana Mparmpagianni
2016

Department of Environmental Science and Analytical Chemistry

Division of Analytical and Toxicological Chemistry

15 Credits
Undergraduate thesis performed at the

Department of Environmental Science and Analytical Chemistry
Division of Analytical and Toxicological Chemistry

Stockholm University

Supervisor: **PhD Christian Baresel (IVL)**
MSc Linda Örtlund (IVL)
Prof Conny Östman (aces)

Table of Contents

Abbreviations

ACES	Environmental Science and Analytical Chemistry
AOP	Advance oxidation process
CAS	Conventional active sludge process
DOM	Dissolved Organic Matter
EPS	Extracellular polymeric substances
GAC	Granulated Activated Carbon
IVL	Swedish Environmental Research Institute
MBBR	Moving Bed Bio Reactor
MBR	Membrane Bioreactor
MF	Microfiltration
MP	Micropollutants
NF	Nanofiltration
$OH^{\cdot}$	Hydroxyl radicals
OM	Organic Matter
PAC	Powdered Activated Carbon
P/C	Protein/carbohydrate ratio
RAS	Return activated sludge
RO	Reversed Osmosis
SRT	Sludge Retention Time or Residence Time for Sludge
STP	Sewage Treatment Plant
TMP	Trans Membrane Pressure
UF	Ultrafiltration
WAS	Wasted activated sludge
WWTP	Wastewater Treatment Plants

Abstract

Increased number of studies over the last years has observed adverse effect from micropollutants (MP), such as pharmaceutical, on wildlife at environmentally relevant concentrations. Wastewater treatment plants are identified as one main source for the discharge of MPs to the recipient. This is because they are collecting the emissions from society but they are not constructed to remove non-degradable organic chemicals. More densely populated cities and stricter emission requirements have increased the demand for more advanced wastewater treatment techniques. The present work is a literature review regarding the possibility of combining membrane bioreactor (MBR), for enhanced removal of suspended solids, with the addition of powdered activated carbon (PAC) as an advanced treatment to remove MPs.

The literature survey showed that addition of PAC in the MBR could result in >80% removal of targeted MPs and an increased removal of organic matter compared to a stand-alone MBR applications. The removal efficiency of MPs seems to be comparable with other advanced treatment techniques, such as granulated activated carbon (GAC) filter columns and ozone treatment. Due to the inherited high removal of MPs, such as antibiotics, by the PAC and the efficient elimination of bacteria by the MBR, the PAC-MBR configuration could facilitate a decrease in spread of bacterial antibiotic resistant genes analogue with oxidative techniques, such as ozone. In addition, the usage of PAC may prolong the operational time of the MBR due to reduced membrane fouling.

The negative effect of the addition of PAC is identified as that the increase in adsorbed organics will elevate the concentration of MPs in settled sludge and further question the usage of sludge as fertilizer on farmland.

Popular Science Abstract

The increased use of chemicals in our everyday lives increases the amount of chemicals that reach our sewage treatment plants. Today's municipal wastewater treatment plants are designed to remove suspended solids and nutrients in the wastewater from re-entering our lakes and waterways to prevent the spread of diseases and minimize eutrophication. They are not constructed to reduce chemicals released from our society. Chemicals that my cause severe damage on wildlife and on our environment. However, an ever-growing population in urban areas and stricter emission requirement from policymakers demand for the need of more efficient wastewater treatment. This work is a literature summary of the possibility of removing unwanted chemicals by addition of activated carbon to the wastewater. Carbons that after it have adsorbed the unwanted chemicals can be separated from the clean water using microfiltration.

The literature search showed that the technique is well suited for the removal of undesirable chemicals. It also showed that pharmaceuticals, such as antibiotics, could be effectively removed by the activated carbon and in combination with the separation of bacteria by the filter it will minimize the spread of antibiotic resistance. To decrease the spread of antibiotic resistance is crucial for our possibilities to treat life-threating diseases.

The only negative effect to clean wastewater with carbon is that the carbon containing the undesirable chemicals will instead end up in the sludge and further question the usage of sludge as fertilizer on farmland.

1. Introduction

1.1 Background

Many municipal sewage treatment plants (STPs) around the world face both an increased load due to a growing population as well as more stringent effluent quality requirements. An example is the sewage treatment in Stockholm that is in need of actions due to Sweden's commitment to the Baltic Sea Action Plan and the implementation of the European water framework directive, among others. Innovative solutions for efficient municipal wastewater treatment need to be implemented that at the same time do not require additional space this is, as in Stockholm, difficult or even impossible for some existing STPs surrounded by residential areas. Stockholm Water Company (Stockholm Vatten AB) has therefore decided to upgrade the exiting conventional active sludge (CAS) process to a membrane bioreactor (MBR) by using a membrane separation as replacement for current post-sedimentation. The new process will be the world's largest MBR facility and be able to treat wastewater from 1.6 million person equivalents (by the year 2040).

Today's wastewater treatment commonly using primary, secondary and tertiary treatment is built to separate suspended solids and to reduce degradable dissolved organic matter (DOM), nitrogen and phosphorus, but not to reduce stable or non-biodegradable organic substances (Baresel et al., 2015). With STPs representing the final station of discharges from our society, they many times represent the major source of pharmaceuticals and other emerging pollutants to the environment (Baresel et al., 2015). This is because many pharmaceuticals and other emerging substances pass through todays STPs and end up in the sludge or in the effluent discharged to recipient, depending on their chemical and physical properties (Baresel et al., 2015). Studies have showed the presence of pharmaceutical residues in Swedish environmental water close to and even above concentrations that may cause an adverse effect on the aquatic wild life (Brodin et al., 2013; Fick et al., 2011). The discharge of pharmaceuticals into the environment may also cause effects on higher organisms, such as birds (Schlabach et al., 2013). The most common reported observed effect on wildlife from pharmaceuticals is skewed sex ratio on fish due to exposure to endocrine disruptors, such as residues from contraceptives (Hinfray et al., 2010; Tetreault et al., 2011). However, the most severe threat to human health and our possibilities to treat life-threating diseases is the evolution and dissemination of bacterial antibiotic resistant genes (WHO 2014). Studies have shown that the presence of antibiotics at environmental relevant concentrations can cause the evolution of antibiotic resistant genes in bacteria (Gullberg et al., 2011).

Therefore, it is critical to further develop and implement new treatment technologies to enhance the removal of persistent organic substances to improve the water quality and protect the aquatic environment (Baresel et al., 2015). Combining exiting CAS or MBR with complementary treatment steps is a common approach and various treatment technologies are available and currently developed (see Section 2.3 Advanced micropollutant (MP)). The MBR process may favor some of these technologies because of an already improved treatment by the process itself (Samuelsson et al., 2014; Baresel et al., 2014, 2015). Instead of an additional treatment step, a proposed interesting treatment approach is the combination of activated carbon treatment and the MBR-process, here entitled as PAC-MBR (see section 2.4 The PAC-MBR concept).

1.2 Aim

This thesis provides an in-depth study to compile the latest scientific knowledge regarding the possibility of utilizing addition of powdered activated carbon (PAC) in membrane bioreactor (MBR) treatment plants in order to increase removal efficiencies for pharmaceutical residues and other emerging substances, here named as Micropollutants (MP) in the effluent of sewage treatment plants. The following aspects will be covered in the study:

- Design of PAC-MBR systems.
- Expected removal efficiency of micropollutants and identification of affecting process parameters to be used for optimization.
- Potential effects of PAC-MBR systems on the general treatment.
- Potential effects of PAC-MBR systems on sludge characteristics.
- Advantages and disadvantages of PAC-MBR systems compared to other treatment techniques for the removal of MPs.
- Recommendations and discussion for further investigations and adaptions required for implementation.

1.3 Project plan/literature review

The thesis at Bachelor level of 15 credits is a feasibility study containing a literature review and concept design. The work has been carried out at IVL Swedish Environmental Research Institute and Hammarby Sjöstadsverk in cooperation with the department of Environmental Science and Analytical Chemistry (ACES), Stockholm University. ACES have also been the examining institution of the thesis.

The individual work is based on gathering, reviewing and compilation of the latest knowledge regarding the use of active carbon in water treatment and especially MBR-systems. Both grey and scientific literature is considered.

The work structure in time was as follows:

1. Literature study in the form of review and compilation of reports and scientific literature regarding the latest knowledge of the methodology.
2. Evaluation of the collected material.
3. Summary of the results including discussion and conclusions.

1.4 Limitations

The limitation in the review is the limited availability of studies related to the PAC-MBR system, which is mainly explained by its novelty. Therefore, technical reports regarding the performance and the behavior of the evaluated technique are scares.

2. Municipal wastewater treatment

2.1 Conventional active sludge (CAS)

Although, large variations in the configuration of modern wastewater treatment exist, the majority of the Swedish STPs are based on three treatment steps (Wahlberg et al., 2006). The three steps comprise a primary mechanical treatment step, a secondary biological treatment step and a tertiary chemical treatment step (Fig. 1).

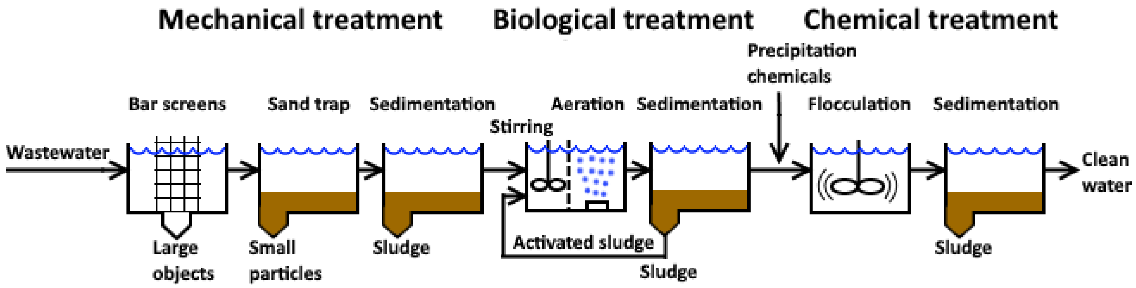

Figure 1: Schematic description of a conventional active sludge (CAS) process.

In the primary step, incoming larger objects, such as napkins, tampons, plastics and food residues etc., are mechanically removed from the raw sewage by bar screens. The sand trap removes smaller particles, like sand, grit and coffee grounds etc. In addition, grease and oil residues are remove in the sand trap or in an own grease/oil separators. The subsequent sedimentation step, also called the pre-sedimentation, consist of a large tank with a low flowrate allowing the sludge to settle. The sludge removed in the pre-sedimentation tank is often digested and turned into biogas (Wahlberg et al., 2006).

The secondary step consists of biological treatment of the wastewater with microorganisms where bacteria digest the organic matter under aerobic conditions and produce carbon dioxide and increased biomass. In addition, bacteria in the biological treatment reduce ammonium compounds to free nitrogen. At first, aerobic bacteria are oxidizing ammonium compounds into nitrite and nitrate (nitrification) and in the following step anaerobic bacteria are reducing nitrite and nitrate to free nitrogen (Wahlberg et al., 2006). After the bacterial treatment, the water is allowed to settle in a sedimentation tank, also known as the secondary clarification. One fraction of the sludge produced in the secondary clarification tank is pumped back to the biological treatment to maintain a sufficient sludge content and carbon source for nitrification (Return activated sludge, RAS) and one fraction is wasted (waste activated sludge, WAS) and often procced to biogas together with the primary sludge.

At last, precipitation of organic matter and phosphorus take place in the tertiary treatment step by addition of coagulation chemicals, such as aluminum, lime, or iron salts (fig 1.). The addition of precipitation chemicals promotes smaller particles to merge or “floc” together into larger particles. The larger masses of particles will settle out in a final sedimentation tank or sand filter (Wahlberg et al., 2006).

2.2 MembraneBioReactor (MBR)

Membrane bioreactor (MBR) combines biological degradation with filtration. The second and third treatment step as described before, are combined into one integrated treatment step. The filters used for water treatment are usually microfilters (MF) with a pore size of 0.1- 0.2 µm or ultrafilters (UF) with a pore size of 0.002- 0.1 µm. The advantage with MBR technique is a disinfection of treated water (Baresel et al., 2015). For example, MFs can retain unicellular organisms, bacteria and turbid particles, while the smaller pore size of UFs offers the added benefit of virus removal (Howell 2004; Samuelsson et al., 2014). The filters, commonly named membranes, are made from either organic polymers or ceramic materials. The polymeric membranes are more cost effective for large-scale applications than ceramic membranes, but may possess larger variations in pore size and are more prone to fouling and deterioration (Scott & Smith 1996). Membranes are manufactured in the format of a flat sheet or as a hollow fiber. Hollow fiber membranes are joined into bundles and submerged in the wastewater. Permeate is drawn through the pores of the wall into the lumen of the fiber by an applied vacuum. Flat sheet membranes are mounted in a cassette. Water flows through the pores of the membrane due to free gravitational flow induced by a pressure difference between the two sides of the sheet. The water flow applied to a membrane can either be cross-flow or dead-end flow. In cross-flow applications, the wastewater is introduced parallel to the membrane surface and the water that does not pass through the membrane pores is recycled and mixed with the feed stream. In dead-end applications, the wastewater is introduced perpendicular to the membrane surface forcing all of the water to pass through the pores of the membrane, or be rejected as waste. Cross-flow is the commonly applied technique in wastewater treatment due to the high water content of particulate matter, which otherwise will promote enhanced fouling in dead-end applications (Alexander et al., 2003).

The MBR modules can be applied in two main configurations; i.e. externally pressurized in a side-stream or submerges directly into the bioreactor. The side-stream pressurized configuration allows for the shutdown of part of the system without interfering with the total treatment and for an easier access to the membrane when it comes to maintenance and cleaning of the tank or the membrane. However, the submerge configuration is more cost effective due to no need for extra pumps to recirculate the activated sludge and space for an additional reaction vessel. Because the high-pressure side of a submerged system is exposed to the atmosphere, the maximum trans-membrane pressure (TMP) is limited. The external pressurized systems are able to operate at a higher TMP than the submerged system, but the enhanced performance rarely justifies the increased energy expenses (Layson 2004).

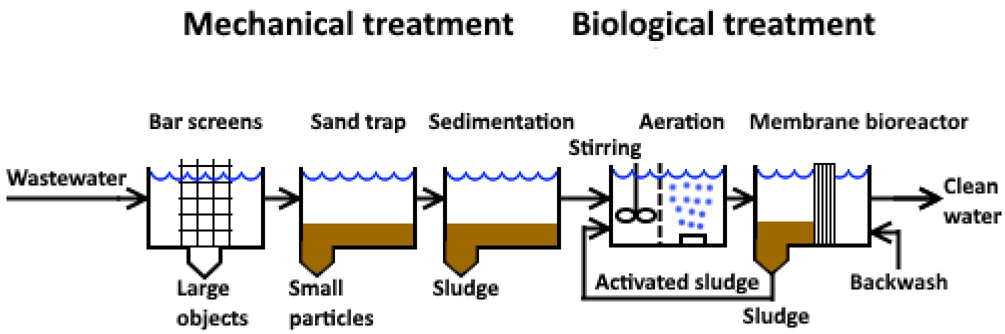

Figure 2: Schematic description of a wastewater treatment process with MBR.

Combining a biological reactor with membrane filtration enhances the removal capacity of particulate and OM residues in the water from the bioreactor compared to a conventional sedimentation basin. As the MBR separates the activated sludge from the water phase more efficient than traditional sedimentation techniques, higher sludge content and a possibility to increase the sludge retention time (SRT) are possible (Samuelsson et al., 2014; Baresel et al., 2015). The advantages with the MBR technology are the high removal efficiency of suspended solids and particulate organic matter resulting in a particle free effluent in a compact process (Samuelsson et al., 2014; Fig. 2). In addition, the MBR effluent will contain less nutrients such as nitrogen and phosphorous compared to conventional sedimentation due to an increased possibility to remove particulate bound organic pollutants (Samuelsson et al., 2014). The high purity of the MBR effluent water will also facilitates for the implementation of additional treatment steps for the removal of MPs, such as pharmaceutical residues and other emerging substances (Samuelsson et al., 2014). The disadvantages with the MBR technique, compared to conventional activated sludge (CAS) processes, are the higher energy demand for aeration and recirculation, and a possible negative effect on the environment due to the increased usage of chemicals to clean the membranes (Samuelsson et al., 2014).

A main concern for the MBR techniques is fouling due to adsorption of OM on the surface of the membrane that causes blockage of the pores, which results in reduced flux and increased TMP over time. To minimize fouling the membranes are operated using cross-flow close to critical flux with subsequent periods of backflush with water and air (Alexander et al., 2003; Howell 2004; Samuelsson et al., 2014). Additional cleaning with oxalic acid, sodium hydroxide or surfactants can also be used if the membrane experience heavy fouling (Samuelsson et al., 2014). The aeration of the membrane with oxygen to promote biodegradation of OM in the reactor has shown to prevent fouling by providing turbulence and scouring effect at the surface of the membrane (Fane 2002). Most MBR system of today for sewage treatment are working in submerge configuration, with outside to inside flow hollow fibers and air/water backwash.

2.3 Advanced micropollutant (MP) removal

Additional advanced treatments targeting MPs are usually located after the three conventional treatment steps in a STP and therefore often called the fourth treatment step. Such treatment can preferably be situated after the traditional treatment such as CAS or MBR as shown for the MBR in Fig. 3. The advanced treatments are used to enhance the removal of organic pollutants from the wastewater further, and are considered when effluent water from a STP reaches sensitive recipients (Sehlén et al., 2015) or enhanced treatment is targeted such as for wastewater reclamation. The commercial available advanced treatment techniques are based on oxidative, prolonged biological or separative treatments (Wahlberg et al., 2006). Especially the high purity of the MBR effluent water facilitates for the implementation of additional treatment steps for the removal of micropollutants (MPs) (Samuelsson et al., 2014).

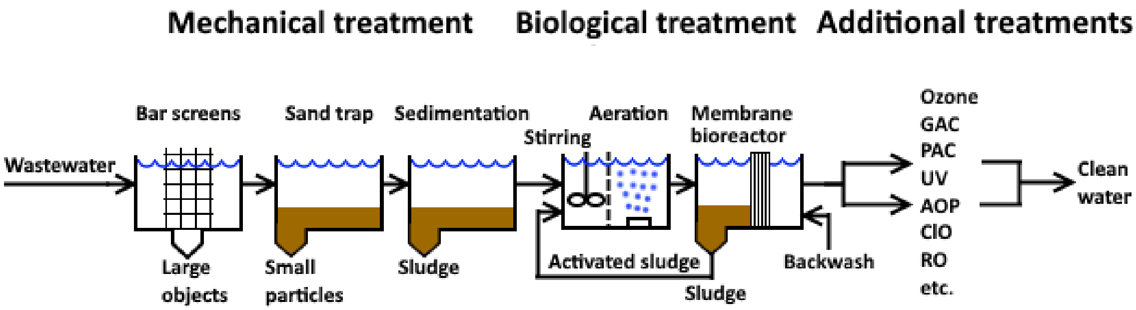

Figure 3: Schematic description of a wastewater treatment process with MBR and advanced MP removal configurations.

Ozonation has under recent years established as the most promising oxidative technique for treatment of sewage water (Baresel et al., 2015). Ozone is generated by passing an electric current through oxygen. When water is treated with ozone, the ozone is decomposed into free hydroxyl radicals ($OH^{\cdot}$). Organic molecules in the water can be oxidized either by the ozone or via the decomposed hydroxyl radicals. Oxidation with ozone is a selective process reacting primarily with double bonds, aromatic systems and un-protonated amines (von Gunten 2003a). In addition, ozone work also as a disinfectant of water and can even inactivate unicellular microorganisms (von Gunten 2003b). Ozone treatment is preferably situated after the biological treatment as the presence of degradable OM otherwise will compete with the more persistent organic pollutants for the oxidative agent (Wahlberg et al., 2006). The main challenge with the technique is to ensure a good mixing and contact of the ozone with the surrounding media (Baresel et al., 2015). The disadvantage with ozone treatment is insufficient mineralization of organic substances transforming them into other degradation products, which can be more or less toxic compared to the parent compound (Baresel et al., 2015).

Other **advanced oxidation process (AOP)** for the treatment of wastewater is UV-light in combinations with, for example, hydrogen peroxide (H_2O_2) or titanium dioxide (TiO_2). These techniques require a relatively particle free and biological treated water and are therefore limited to the tertiary treatment step (Baresel et al., 2015).

Chlorine dioxide (ClO_2) is also an oxidative treatment technique widely used as a disinfectant in public water system, such as drinking water and swimming pools (Baresel et al., 2015). However, the low removal efficiency of pharmaceuticals with high electron-withdrawing moieties will limit the implementation of the technique in sewage wastewater treatment (Hey et al., 2012).

Granulated activated carbon (GAC) packed in a column for filtration of water is the most frequently used separative treatment technique to remove organic pollutants from sewage water. Activated carbon is a solid porous material with a large surface area (1000-1500m^2/g) and a porosity of >80% with high capacity to adsorb OM (Lesage et al., 2008). The carbon is activated through combustion in the presence of vaporised water (Wahlberg et al., 2006). The activated carbon has a large affinity to high molecular weight compounds and hydrophobic compounds (Wahlberg et al., 2006). The GAC filter column is preferably situated after the MBR, or after similar membrane filter, otherwise the presence of particulate matter in the water phase tends to clog the carbon filter over time resulting in increased backpressure of the column (Ek et al., 2014).

In addition, **Powder activated carbon (PAC)** may be used as a tertiary treatment step in a separate reactor. However, this requires that an additional separation step has to be included, often followed by a final filtration with e.g. sand filter, to avoid activated carbon discharges to the recipient.

After exhausted use, the surface of the activated carbon will be saturated with organic compounds and needs to be regenerated through incineration of the adsorbed organics (Aktas & Cecen 2007). The main advantage of using activated carbon for water treatment, compared biological and oxidative methods is the total removal of the priority substance without transforming it into other degradation products (Baresel et al., 2015). On the other hand, no disinfection of the treated water can be achieved by utilizing activated carbon alone.

There exists a variety of commercial available **prolonged biological treatment** techniques. All techniques aim to prolong the sludge retention time (SRT) to enhance the bacterial degradation of OM (Wahlberg et al., 2006). One of the techniques is the activated sludge process where flocs of mainly aerobe bacteria are kept suspended in the water phase by aeration. The suspended configuration of the flocs in combination with the oxygen rich environment will favor the bacterial contact surface with the surrounding matrix and enhance the aerobic degradation (Wahlberg et al., 2006). Another technique is the MBR treatment, which combines a biological reactor with membrane filtration. Combining the two techniques enhances the removal capacity of particulate and organic matter residues in the water from the bioreactor compared to a conventional sedimentation basin. The enhanced removal of biological material will result in an increased residence time for sludge (SRT) and microorganisms, which will promote enhanced sludge digestion (Wahlberg et al., 2006). For additional information, regarding the MBR configuration, see pervious section. The moving bed bioreactor (MBBR) is another prolonged biological treatment. In contrast to the two previous mentioned biological treatment configurations is the bacteria, involved in the degradation of OM in the MBBR, attached to floating polymeric carrier material that is kept suspended through aeration or through stirring. The advantage of attaching the bacteria to carrier materials is that the microorganisms become more protected and less vulnerable for fluctuations in the sewage water (Wahlberg et al., 2006).

Membrane filter technologies can also be applied as a tertiary treatment step to treat wastewater. The most common techniques are micro-(MF), ultra-(UF), Nanofiltration

(NF) and reversed osmosis (RO). However, besides disinfection and the removal of suspended particles and particle bound substances, micro- and ultrafiltration is not effective in removing MPs (Baresel et al., 2015). According to Wahlberg et al., (2010) it requires the use of RO to show high removal efficiency of pharmaceuticals. However, the technique is commonly used in drinking water treatment due to the restricted flowrate through the RO membrane (Baresel et al., 2015), which implies high treatment costs.

2.4 The PAC-MBR concept

One other possibility for advanced treatment is the addition of powdered activated carbon (PAC) in secondary treatment. This implies that the PAC will end up in the WAS and thus negatively affect the possibilities of using sludge. Regeneration also becomes more difficult as the separation of PAC and biosolids is difficult in traditional CAS-systems. However, addition of PAC in the MBR process, here referred to as PAC-MBR, to attract/adsorb the presence of organic pollutants in the water phase may be a potential approach as the organic contaminants adsorbed by the PAC particles can thereafter be separated along with other particulate materials in the MBR. This could effectively enhance the removal efficiency of organic compounds (Nguyen et al., 2013). However, several questions need to be investigated and optimized before the PAC-MBR configuration can be fully integrated.

3. Assessment/evaluation of the PAC-MBR

3.1 Design of PAC-MBR systems

The PAC-MBR treatment technique can be described as a hybrid process where the micropollutants together with other DOM, normally not retained by the membrane filter, are adsorbed by the PAC particle added to the wastewater. Thereafter, the suspended PAC particles with the adsorbed micropollutants are separated from the water phase by the membrane filter (Fig. 4). PAC is usually added as hydrated slurry when fed frequently into a water system (Campos et al., 2000b; Westerhoff et al., 2005). The addition of the PAC particles to the water phase could be done using two configurations; either through a continuous dosing or by dosing all the PAC required in one addition (pulse input), for example during the membrane backwash (Campos et al., 2000a). Using the continuous dosage configuration, the PAC concentration present in the water phase will be constant throughout the process and thus also the removal of organic compounds. When all the PAC is added at once (pulse input), the organic content in the permeate will drop dramatically shortly after the addition and thereafter increase over time due to decrease of the adsorptive capacity of the PAC.

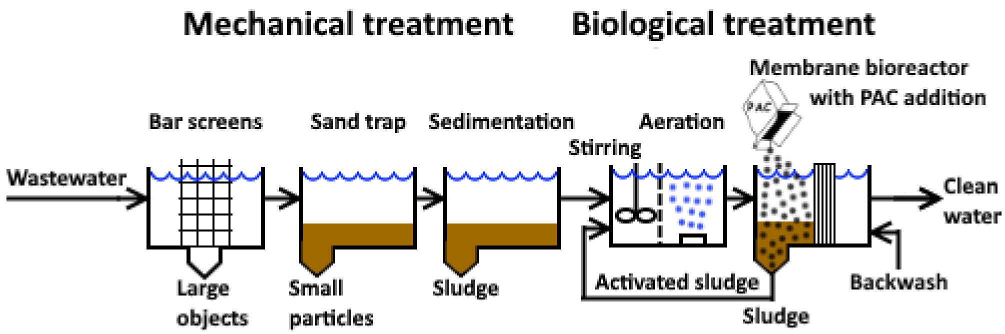

Figure 4: Schematic description of a wastewater treatment process with addition of PAC in MBR.

3.2 Expected removal efficiency

Activated carbon is a solid porous adsorptive material with a large surface area (1000-1500m^2/g) and a porosity of >80% (Lesage et al., 2008). Organic compounds are mainly retained by specific interactions with functional groups at the surface of the activated carbon, such as electrostatic and hydrophobic interactions (Margot et al., 2013; Löwenberg et al., 2014). The removal efficiency of organic pollutants with the additional of PAC is not exclusively governed by adsorption, but rather a combination between adsorption and biodegradation, i.e. mechanisms independent of each other (Orshansky & Narkis 1997). Several studies have reported an observed increase in microbial metabolism of organic pollutants (Orshansky & Narkis 1997; Lesage et al., 2008), OM (Vigneswaran et al., 2003; Guo et al., 2008; Satyawali & Balakrishnan 2009a; Lin et al., 2011) and nitrates (Lin et al., 2011; Yamashita & Yamamoto-ikemoto 2014). The shared explanation has been the increased surface area available for bacterial growth in the presence of suspended PAC in wastewater. In addition, it is assumed that the enhanced biodegradation of adsorbed organics by microbes at the surface of the carbon will result in a continuous regeneration of the PAC material (Vigneswaran et al., 2003; Satyawali & Balakrishnan 2009a). The enhanced removal of biological material will result in an increased residence time for sludge (SRT) and microorganisms, which will promote enhanced biodegradation of organic pollutants provided that a good aeration of the produced sludge can be maintained (Wahlberg et al., 2006). However, the presence of halogens (Kimura et al., 2005) or nitrogen (Orshansky & Narkis 1997; Kimura et al., 2005) in the molecule structure can protect the organic compound from bacterial biodegradation. By returning part of the produced activated sludge from the MBR, containing PAC, it is possible to recirculate and keep a higher PAC content suspended in the biological treatment process for enhanced MPs removal until it is saturated.

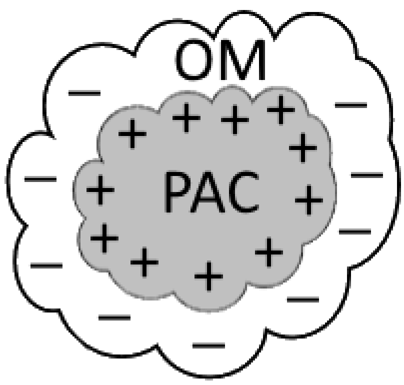

Figure 5: PAC particle saturated with organic matter (OM).

Removal efficiencies of the MBR-process in general and the PAC-MBR process in specific may further have a substantial potential for further optimisations as studies with prolonged biological treatment indicate (e.g. Wahlberg et al., 2006). This may include adjustments of e.g. sludge retention time (SRT) and sludge concentration. Adjustment of the individual processes of biology, filtration and PAC towards each other may facilitate increased removal efficiencies.

3.3 Impact on general MBR treatment efficiency

Other sorption mechanisms, such as hydrogen bond formation, pi-pi interactions and Van deer Waals forces, may dominate the PAC adsorption for molecules with low hydrophobicity (de Ridder et al., 2010). Although adsorptive materials with specific interactions are to be preferred in certain designs, there is always the risk of saturating the fixed number of bonding sites when applied to a complex matrix. The saturation of the surface leads to competition between organic compounds for the limited number of bonding sites resulting in non-linear concentration isotherms (Schwarzenbach et al., 2003), which will complicate the estimated removal efficiency of a target compound in real applications. At pH 7 the surface of the fresh activated carbon is neutral or slightly positively charge (Margot et al., 2013), suggesting that hydrophobic and/or acidic (negatively charge) compound would be adsorbed and successively removed from the water phase by the addition of PAC. However, the relative abundance of organic matter (OM) in the wastewater, known to be negatively charge (Haderlein et al., 1993; Magnér et al., 2009), will compete with the organic pollutants for the sorptive sites at the surface of the PAC and create a slightly negatively charge boundary layer (Margot 2013) (Fig. 5). The result of the existence of a negatively charge layer give an expected high removal efficiency of basic (positively charge) compounds, followed by the removal of hydrophobic compounds and a low removal efficiency of acidic (negatively charge) compounds. This adsorptive characteristic has been confirmed in several studies (Westerhoff et al., 2005; de Ridder et al., 2010; Margot et al., 2013; Löwenberg et al., 2014). The presence of a negatively charge boundary layer on activated carbon have also been the leading explanation in the scientific literature for the high removal observed for cationic heavy metals in wastewater, with an optimal condition of removal efficiency around pH 6 to 7 (Hema et al., 2010; Hegazi 2013). Matsui et al., (2003), showed that the pores of the activated carbon was not blocked or restricted by the formed boundary layer, which otherwise would have reduced the overall adsorptive performance of the carbon, but that OM with similarities in size and structure as the targeted organic pollutants rather competed for the sorptive sites (Yu et al., 2008).

Studies regarding the impact of PAC on membrane operation seem to be unanimous that an addition of PAC in the water phase prior to the MBR will result in more stable transmembrane pressure (Guo et al., 2008; Remy et al., 2009; Lin et al., 2011). This result in a prolonged operational time (Lesage et al., 2008; Remy et al., 2009; Satyawali & Balakrishnan 2009a, 2009b; Lin et al., 2011) compared to MBR systems without addition of PAC. However, disagreements exist when it comes to the effect of PAC addition on membrane filtration flux. From a slight improvement over time (Remy et al., 2009; Satyawali & Balakrishnan 2009a), to no observed effect (Campinas & Rosa 2010), to an observed deterioration in critical flux (Guo et al., 2008), which could be a result of differences between types of water selected to evaluate the membrane technique in the different studies. Important for the purpose of this report is to mention that one of the studies, reporting an improved flux over time due to the addition of PAC, was performed on a municipal wastewater (Remy et al., 2009). A common explanation in the scientific literature for the prolonged operational time is the positive effect the addition of PAC can have on reducing the membrane fouling. Several mechanisms have been suggested to explain the phenomena. For example that PAC could serve as a coagulant adsorbing organic substances, such as OM, proteins, carbohydrates and free bacterial cells (Tomaszewska & Mozia 2002; Guo et al., 2008, Lesage et al., 2008; Satyawali & Balakrishnan 2009a; Campinas & Rosa 2010; Lin et al., 2011), substances that otherwise would have been adsorbed on the surface of the membrane and caused increased fouling. Another explanation is that particles of PAC in combination with the aeration of the membrane filter provide an extra scouring of the filter surface mitigating fouling (Satyawali & Balakrishnan 2009b; Löwenberg et al., 2014). An additional explanation to the improved operational time could be that the addition of PAC will result in a more porous non-compressible cake and gel layer on the surface of the membrane. This layer would have a higher filterability and would be easier to remove during cleaning, i.e. backwash to restore the filter capacity, than cake formation built up during absence of PAC in the water phase (Tomaszewska & Mozia 2002; Remy et al., 2009; Teychene et al., 2011). However, Tomaszewska & Mozia (2002) showed that removing of the cake formation and restoring the initial flux using backwash was only effective when <20 mg of PAC/L water was applied.

A positive effect by the addition of suspended PAC in the MBR worth mentioning is that PAC appears to act as a carrier material protecting bacteria and microorganisms from sudden toxic impulses reaching the treatment making the process less vulnerable and more stable over time (Lesage et al., 2008).

3.4 Advantages and disadvantages of PAC-MBR systems compared to other advanced treatment techniques for the removal of MPs

An obvious advantage is that no additional treatment step is required in order to accomplish an enhanced removal of MPs. On the other hand, PAC addition requires a different approach of sludge handling and loaded PAC in WAS will prevent e.g. in Sweden commonly applied sludge fertilizing.

In traditional STP, using active sludge process can potentially degrade all organic substances by an enhanced biological treatment process (Suárez et al., 2008). This can be achieved through an addition of carrier materials, for increased bacterial growth, or by increasing the SRT. However, enhancement in biological degradation in conventional active sludge process will inevitably result in increased process volumes, which is not the case in an MBR system (Baresel et al., 2015).

Margot et al., (2013) showed in large pilot scale experiments that PAC addition in combination with MBR was as feasible as the more common ozone treatment technique. This is according to the study valid for long-term treatment and removal of trace contaminants in wastewater, under the experimental prerequisites. Further, similar expenditure costs as for the treatment with ozone were predicted if the membrane filter was substituted with a sand filter for the separation of PAC. Torretta et al., (2013) showed that an addition of between 2 to 5 mg/L PAC significantly improved membrane performance, such as an increase in membrane permeate flux of 27% over time, reduction in energy consumption due to mitigation of TMP increase and less cleaning cycles of the membrane. The study also showed that further addition of PAC above 5 mg/L did not lead to any additional benefits. A study confirming this finding revealed that PAC addition of less than 20 mg/L improved the membrane performance after backwash, while addition of PAC above 20 mg/L the initial flux was not recovered (Tomaszewska & Mozia 2002). Studies have also showed that addition of PAC as pulse input, instead of continuously, enhanced the removal of organic constituents in the membrane permeate and increase the operational time of the membrane between wash cycles (Campos et al., 2000b; Vigneswaran et al., 2003). Satyawali & Balakrishnan (2009b) observed that addition of PAC to the MBR lead to little or no foaming, while MBR without addition of PAC experienced severe foaming and had to be dosed frequently with antifoaming agent. The finding means that PAC addition could minimize costs associated with foaming control at STPs. They also observed that addition of PAC lead to an enhancement in buffering capacity of the system when handling increased organic loads. It is important to stress that PAC-MBR system for wastewater applications are strongly dependent of a variety of factors that needs to be optimized, such as backwashing frequencies, size of the reactor, filtration configuration and dosing procedures. However, some of the basic feature of the MBR configuration could work in favor for the addition of PAC, such as the aeration of the membrane that will keep the PAC particles suspended (Guo et al., 2008; Löwenberg et al., 2014).

A comparison in the removal efficiency of organic pollutants spiked to synthetic wastewater between a GAC filter column, following MBR treatment (MBR-GAC), and suspended PAC, added to the MBR (PAC-MBR), showed that the PAC-MBR outperformed the MBR-GAC with regards to treated volume, under the predefined experimental conditions (Nguyen et al., 2013). The higher removal efficiency of organic pollutants was dedicated, in the study, to the higher surface area per unit weight of PAC compared to GAC. The study also revealed that the MBR alone had negligible impact on the removal of the more hydrophilic and biological persistent pollutants. An additional disadvantage with the GAC filter column application compared to the PAC-MBR technique is that the adsorption capacity of the column will decline and that the presence of particulate matter in the water phase tends to clog the carbon filter over time and is therefore in need of regular regeneration (Ek et al., 2014). However, the regeneration of the GAC material through incineration is a destructive treatment technique that will destroy all adsorbed organic pollutants before reuse of the GAC material (Aktas & Cecen 2007). Ozone treatment will also lead to elimination of the organic pollutants it degraded and prevent it from re-entering the water or sludge phase. In contrast to GAC filter column and ozone treatment the PAC particles are impossible to separate from the sludge and the adsorbed organics will elevate the presence of organic pollutants in settled sludge (Ek et al., 2014; Baresel et al., 2015; US EPA), which would further question the usage of sludge as fertilizer on farmland. Incineration of the produced sludge from PAC-MBR treatment would be the only way to prevent adsorbed organic pollutants from re-entering the recipient (Aktas & Cecen 2007). The main advantage of using activated carbon for water treatment, compared to biological and oxidative methods, is the total removal of the priority substance without transforming it into other, perhaps more toxic, degradation products (Baresel et al., 2015).

Two studies comparing the removal efficiency of organic micropollutants in effluent wastewater between ozone, at dosage of 5 to 7 mg/L, and suspended PAC, at dosage of 10 to 20 mg/L, revealed an equivalent average removal between the two techniques of above >80% for the micropollutants investigated (Margot et al., 2013; Altmann et al., 2014). However, the removal efficiency by ozone appeared to be more substance dependent than the removal by PAC. Ozone was more effective in removing micropollutants with electron-rich moieties, while adsorption to PAC was more general with preference for hydrophobic or positively charged compounds (Margot et al., 2013). Altmann et al., (2014) showed that both techniques effectively removed DOM, with a slight better correlation between the DOM removal and the relative MP removal by PAC, and that UV-absorbance at 254 nm can be used as representative for the overall MP removal. Margot et al., (2013), with an extensive set of different toxicity test at two tropical levels (algae and fish) and additional estrogenic test, showed that ozone and PAC-MBR effluent resulted in clear reduction in toxicity compared to conventional treated effluent, with PAC slightly performing better overall. Although, there are several articles in the scientific literature showing an increased toxicity after ozone treatment compared to treatment with activated carbon (Stalter et al., 2010; Magdeburg et al., 2012). One complication to the PAC-MBR treatment process is the potential re-growth of microorganisms due to small, but still sufficient, amount of biodegraded DOM and nutrients in the reclaimed water after the MBR and the use of chlorine disinfection to prevent the transmission of pathogenic microorganisms, which can promote the formation of toxic trihalomethanes (Ma et al., 2014). However, the drawback with oxidative treatment techniques, such as ozone, is insufficient mineralization of organic substances transforming them into other degradation products, which can be more or less toxic compared to the parent compound (Baresel et al., 2015).

To minimize the evolution and dissemination of bacterial antibiotic resistant genes to the environment it is important remove both bacteria and antibiotic residues in the effluent wastewater (Baresel et al., 2015). Oxidative treatment techniques such as ozone can eliminate bacteria and antibiotics (Baresel et al., 2015). Filtration techniques, such as membrane microfilters, can remove bacteria but may not guarantee complete removal of antibiotic residues. On the other hand, adsorptive techniques, such as PAC or GAC, are not an effective disinfection of the wastewater (Baresel et al., 2015). However, by combining PAC addition to MBR, both bacteria and antibiotics could be removed from the wastewater, without any remaining transformation or degradation byproducts as seen utilizing oxidative treatment techniques (Baresel et al., 2015).

A further advance of the PAC-MBR system is the potential for further optimisations for resources-effective treatment when considering adjustments of the individual processes of biology, filtration and PAC towards each other.

3.5 Impact on sludge characteristics

Reports in the scientific literature, regarding chemical and physical appearance of sludge after the addition of PAC, are scare and not consistent. For example, Lesage et al., (2008) noticed a decrease in sludge production with addition of PAC, while Margot et al., (2013) reported an increase in sludge production with increased dosages of PAC. However, it seems that the presence of suspended PAC in the water phase may improve the settleability and dewaterability of sludge in the MBR (Satyawali & Balakrishnan 2009b). A reason for that is the observed change in wastewater composition of extracellular polymeric substances (EPS) upon addition of PAC. EPS consist of high molecular proteins and carbohydrates (polysaccharides). They are excreted from the cell under normal bacterial growth and metabolism. The function of the EPS matrix includes aggregation of bacterial cells in flocs and biofilms, formation of a protective barrier around the bacteria, retention of water and adhesion to surfaces. The addition of PAC increased the protein/carbohydrate (P/C) ratio in wastewater compared to a stand-alone MBR configuration. The high P/C ratio implies improved settleability and dewaterability of sludge due to the hydrophobic nature of proteins (Satyawali & Balakrishnan 2009b).

However, more studies are needed in order to clarify if this is the case. The drawback with addition of PAC in sewage treatment is that, although it improves the removal of organic pollutants from the effluent water through adsorption, it will elevate the presence of organic pollutants in settled sludge, which would further question the usage of sludge as fertilizer on farmland (Ek et al., 2014; Baresel et al., 2015; US EPA).

4. Discussion

Treating sewage water using MBR techniques is quite energy demanding and the enhanced treatment performance including high removal efficiency of suspended solids and particulate organic matter resulting in a more particle free effluent from a more compact process (Samuelsson et al., 2014) compared to conventional activated sludge techniques, may not always justifies the increase in energy expenses. However, with increased emission requirements from an ever-growing population, beside general treatment improvements it is also of great concern to look at additional treatment techniques to reduce emissions of MPs, especially when effluent water from a STP is discharged into a sensitive recipient (Sehlén et al., 2015). Addition of PAC as an advanced treatment in MBR seems to be an effective technique to removal organic pollutants from wastewater as presented in this review.

Although, many public reports and scientific literature evaluating the implementation of the PAC-MBR technique in wastewater treatment were identified, it is still difficult to compare the PAC-MBR system to other technologies. This is mainly because of differences in the prerequisites between the different experimental set-ups such as e.g.:

- Type of water used; industrial, synthetic or sewage wastewater.
- Type of membrane used; flat sheet or hollow fibre.
- Submerged or pressurised membrane operation.

- Characteristic of the PAC used.
- Applied concentration of PAC.
- PAC exposure time in the media.
- Pilot scale or a laboratory scale experiment.
- Types of MPs investigated.
- Type of samples taken; grab or composite sample, sample frequency.
- Etc.

Another uncertainty in the evaluation between different PAC-MBR configurations are measurement errors that will occur when analysing organic substances in complex matrices, like wastewater. Impurities from the matrix can co-elute with the substance of interest during the mass spectrometric determination causing ion suppression or ion enhancement. This matrix effect will mask the true concentration of the target analyte in the sample and complicate the quantification (Baresel et al., 2015). This is mostly not described or discussed in published studies but is a well-recognised problem especially for substances such as MP at low concentrations (Baresel et al., 2015).

Further research need to be done in pilot scale applications with the same experimental condition and with the same set of target analytes in order to evaluate operational performance of the technique and to be able to compare it with other advanced treatment techniques for the removal of MPs.

5. Conclusions and recommendations

The conclusion of the review of PAC-MBR system is that it is a promising advanced treatment technique for the removal of MPs in sewage wastewater. The advantages with the PAC-MBR technique compared to a stand-alone MBR application and other CAS systems combined with or without advanced treatment systems targeting the removal of MP are:

- High removal of MPs (>80%).
- Increased biodegradation of MPs, organic matter (OM) and nitrates.
- Potential to minimize bacterial antibiotic resistance in the effluent by removing both bacteria and, through the PAC addition, the antibiotic residues.
- Increased settleability and dewaterability of the produced sludge.
- Prolonged operational time reduced membrane fouling and a more porous non-compressible cake formation on the surface of the membrane.
- The suspended PAC acts as a carrier material protecting bacteria and microorganisms from sudden toxic impulses reaching the treatment making the process less vulnerable and more stable over time.

The limitations with the PAC-MBR technique compared to a stand-alone MBR application are:

- Increased costs due to the addition of PAC.
- That the PAC particles are impossible to separate from the sludge and the adsorbed organics will elevate the presence of organic pollutants in settled sludge, which would further question the usage of sludge as fertilizer on farmland.

The literature provides some basic recommendations on the system integration of PAC-MBR:

- Addition of PAC less than <20 mg/L wastewater improved membrane performance, and that addition of >20 mg/L could result in that the initial flux was not restored during backflush due to irreversible cake formation.
- Addition of PAC as pulse input, instead of continuously, enhanced the removal of organic constituents due to prolonged exposure time for the PAC in the media.
- To facilitate for an even distribution of the adsorbent PAC should preferably be fed to the system as a hydrated slurry.
- PAC removal of DOM corresponds well with the removal of MPs, which means that on-line measurements of UV-absorbance at 254 nm can be used to operate the system.
- The elevated concentration of MPs in the settled sludge with addition of PAC implies that the produced sludge should preferably be incinerated rather than reused as fertilizer on farmland.

6. Perspectives

6.1 Societal perspectives

Pharmaceutical residues have been detected in surface water in most part of the world. Reports have shown that the presence of pharmaceuticals can cause adverse effect on natural wild life, such as skewed gender distribution and even behavioral changes on fish. However, the most severe threat to human health and our possibilities to treat life-threating diseases is the evolution and dissemination of bacterial antibiotic resistance genes. Besides production sites for pharmaceuticals as point sources, sewage treatment plant (STP) effluents representing the main source of discharges from our society. This is because many pharmaceuticals consumed by humans pass through todays STPs and end up either in the sludge or in the effluent. Significant effort is invested into research and exploitation of upstream measures to reduce the discharge of pharmaceuticals. However, because human health and patient safety are of primary interest, the environment of secondary concern, upstream measures are limited in reducing the discharges of pharmaceuticals. Therefore, it is critical to develop and implement advanced wastewater treatment technologies, such as PAC-MBR, to improve the water quality and protect the aquatic environment.

6.2 Research perspectives

During the development of an advanced wastewater treatment process, it is important to evaluate the quality of the produced sludge and effluent so that no transformation or degradation byproducts are being formed that may cause future adverse effect on the environment.

Considering the novelty of the PAC-MBR approach, potential for further optimisations towards a resources-effective treatment exits but more research is necessary to define such optimisation potential.

7. References

Aktas Ö, *Ḉeḉen F*, *Bioregeneration of activated carbon: A review*, Int. Biodeter. Biodegr. 59 (**2007**) 257–272.

Alexander K, Guendert D M, Pankratz T M, *Comparing MF/RO Performance on Secondary and Tertiary Effluents in Reclamation and Reuse*. International Desalination (**2003**) Association Conference Proceedings.

Altmann J, Ruhl A S, Zietzschmann F, Jekel M, *Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment,* Water Res. 55 (**2014**) 185-193.

Baresel C, Ek M, Ejhed H, Harding M and Bergström R, *Behandling av biologiskt renat avloppsvatten med ozon eller aktivt kol.* IVL Svenska Miljöinstitutet AB (**2014**), IVL-rapport B 2203.

Baresel C, Palm Cousins A, Hörsing M, Ek M, Ejhed H, Allard A-S, Magnér J, Westling K, Wahlberg C, Fortkamp U, Söhr S, *Pharmaceutical residues and other emerging substances in the effluent of sewage treatment plants. Review on concentrations, quantification, behaviour, and removal options*, IVL Swedish Environmental Research Institute Ltd (**2015**), IVL-report B 2226.

Brodin T, Fick J, Jonsson M, Klaminder J, *Dilute Concentrations of a Psychiatric Drug Alter Behavior of Fish from Natural Populations,* Science 339 (**2013**) 814-815.

Campinas M, Rosa M J, *Assessing PAC contribution to the NOM fouling control in PAC/UF systems,* Water Res. 44 (**2010**) 1636-1644.

Campos C, Mariñas B J, Snoeyink V L, Baudin I, Lainé J M, *PAC-Membrane Filtration Process. I: Model Development*, *J. Environ. Eng.*, ASCE 126 (**2000a**) 97-103.

Campos C, Mariñas B J, Snoeyink V L, Baudin I, Lainé J M, *PAC-Membrane Filtration Process. II: Model Application*, *J. Environ. Eng.*, ASCE 126 (**2000b**) 104-111.

de Ridder D J, Villacorte L, Verliefde A R D, Verberk J Q J C, Heijman S G J, Amya G L, van Dijk J C, *Modeling equilibrium adsorption of organic micro pollutants onto activated carbon,* Water Res. 44 (**2010**) 3077 – 3086.

Ek M, Baresel C, Magnér J, Bergström R, Harding M, *Activated carbon for the removal of pharmaceutical residues from treated wastewater,* Water Sci. Technol. 69 (**2014**) 2372-2380.

Fane A G, *Membrane bioreactors: design & operational options.* Filtr. Sep. 39 (**2002**) 26-29.

Fick J, Lindberg R H, Kaj L, Brorström-Lundén E, *Results from the Swedish National Screening Programme 2010, Subreport 3. Pharmaceuticals*, IVL Swedish Environmental Research Institute Ltd (**2011**), IVL-report B 2014.

Gullberg E, Cao S, Berg O G, Ilbäck C, Sandegren L, Hughes D, Andersson D I, *Selection of Resistant Bacteria at Very Low Antibiotic Concentrations.* PLoS Pathog (**2011**) 7(7): e1002158. doi:10.1371/journal.ppat.1002158.

Guo W, Vigneswaran S, Ngo H-H, Xing W, Goteti P, *Comparison of the performance of submerged membrane bioreactor (SMBR) and submerged membrane adsorption bioreactor (SMABR),* Bioresour. Technol. 99 (**2008**) 1012-1017.

Haderlein SB, Schwarzenbach RP, *Adsorption of substituted nitro-benzenes and nitrophenols to mineral surfaces*, Environ. Sci. Technol. 27 (**1993**) 316–326.

Hegazi H A, *Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents,* HBRC Journal 9 (**2013**) 276–282.

Hema M, Srinivasan K, *Uptake of toxic metals from wastewater by activated carbon from agro industrial by-product*, Indian J. Eng. Mater. Sci. 17 (**2010**) 373-381.

Hey G, Grabic R, Ledin A, la Cour Jansen J, Andersen H R, *Oxidation of pharmaceuticals by chlorine dioxide in biologically treated wastewater,* Chemical Engineering Journal 185–186 (**2012**) 236-242.

Hinfray N, Palluel O, Piccini B, Sanchez W, Aït-Aïssa S, Noury P, Gomez E, Geraudie P, Minier C, Brion F, Porcher J-M, *Endocrine disruption in wild populations of chub (Leuciscus cephalus) in contaminated French streams*, Sci. Total Environ. 408 (**2010**) 2146-2154.

Howell J A, *Future of membranes and membrane reactors in green technologies and for water reuse,* Desalination 162 (**2004**) 1–11.

Kimura K, Hara H, Watanabe Y, *Removal of pharmaceutical compounds by submerged membrane bioreactors (MBRs),* Desalination 178 (**2005**) 135-140.

Layson A, *Impact of Water Technology Developments on Economics of Water Recycling and Reclamation in the Power Industry*, Memcor Technology Centre (**2004**), www.usfilter.com

Lesage N, Sperandio M, Cabassud C, *Study of a hybrid process: Adsorption on activated carbon/membrane bioreactor for the treatment of an industrial wastewater*, Chem. Eng. Process. 47 (**2008**) 303–307.

Lin H, Wanga F, Dinga L, Honga H, Chena J, Lub X, *Enhanced performance of a submerged membrane bioreactor with powdered activated carbon addition for municipal secondary effluent treatment,* J. Hazard. Mater. 192 (**2011**) 1509– 1514.

Löwenberg J, Zenker A, Baggenstos M, Koch G, Kazner C, Wintgens T, *Comparison of two PAC/UF processes for the removal of micro pollutants from wastewater treatment plant effluent: Process performance and removal efficiency,* Water Res. 56 (**2014**) 26 - 36.

Ma D, Gao B, Xia C, Wang Y, Yue Q, Li Q, *Effects of sludge retention times on reactivity of effluent dissolved organic matter for trihalomethane formation in hybrid powdered activated carbon membrane bioreactors*, Bioresour. Technol. 166 (**2014**) 381-388.

Magdeburg A, Stalter D, Oehlmann J, *Whole effluent toxicity assessment at a wastewater treatment plant upgraded with a full-scale post-ozonation using aquatic key species*, Chemosphere 88 (**2012**) 1008–1014.

Magnér J A, Alsberg T E, Broman D, *The ability of a novel sorptive polymer to determine the freely dissolved fraction of polar organic compounds in the presence of fulvic acid or sediment,* Anal. Bioanal. Chem. 395 (**2009**) 1525-1532.

Margot J, Kienle C, Magnet A, Weil M, Rossi L, de Alencastro L-F, Abegglen C, Thonney D, Chèvre N, Schärer M, Barry D A, *Treatment of micro pollutants in municipal wastewater: Ozone or powdered activated carbon?* Sci. Total Environ. 461–462 (**2013**) 480–498.

Matsui Y, Fukuda Y, Inoue T, Matsushita T, *Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanism of competitive adsorption*, Water Res. 37 (**2003**) 4413- 4424.

Nguyen N L, Hai F I, Kang J, Nghiem L D, Price W E, Guo W, Ngo H H, Tung K-L, *Comparison between sequential and simultaneous application of activated carbon with membrane bioreactor for trace organic contaminant removal,* Bioresour. Technol. 130 (**2013**) 412-417.

Orshansky F, Narkis N, *Characteristics of Organics Removal by Pact Simultaneous Adsoption and Biodegradation*, Wat. Res. 31 (**1997**) 391-398.

Remy M, van der Marela P, Zwijnenburga A, Rulkensb W, Temminka H, *Low dose powdered activated carbon addition at high sludge retention times to reduce fouling in membrane bioreactors,* Water Res. 43 (**2009**) 345-350.

Samuelsson O, Royen H, Ottosson E, Baresel C, Westling K, Bergström R, Bengtsson L, Yang J-J, Dahlén N, Laurell C, Lindblom E, Grundestam J, *Pilotförsök med membranreaktor för avloppsvattenrenin, Delrapport 1 – Försöksår 1,* IVL Svenska Miljöinstitutet AB (**2014**), IVL-rapport B 2215.

Satyawali Y, Balakrishnana M, *Performance enhancement with powdered activated carbon (PAC) addition in a membrane bioreactor (MBR) treating distillery effluent,* J. Hazard. Mater. 170 (**2009a**) 457-465.

Satyawali Y, Balakrishnana M, *Effect of PAC addition on sludge properties in an MBR treating high strength wastewater,* Water Res. 43 (**2009b**) 1577-1588.

Schwarzenbach R P, Gschwend P M, Imboden D M, *Environmental Organic Chemistry*. *Second ed., John Wiley & Sons Inc*. (**2003**) Hoboken, New Jersey, USA**.**

Schlachbach M, Haglund P, Rostkowski P and Dye C, *Non-target screening – A powerful tool for selecting environmental pollutants*, Rapport M-27/(**2013)** Miljødirektoratet.

Scott J A, Smith K L, *A Bioreactor Coupled to a Membrane to Provide Aeration and Filtration in Ice-Cream Factory Waste Water*, Water Resour. Res, 31 (**1996**) 1, 69.

Sehlén R, Malmborg J, Baresel C, Ek M, Magnér J, Allard A-S, Yang J, *Pilotanläggning för ozonoxidation av läkemedelsrester i avloppsvatten*, IVL Svenska Miljöinstitutet AB (**2015**), IVL-rapport B 2218.

Stalter D, Magdeburg A, Weilb M, Knacker T, Oehlmann J, *Toxication or detoxication? In vivo toxicity assessment of ozonation as advanced wastewater treatment with the rainbow trout*, Water Res. 44 (**2010**) 439-448.

Suárez S, Carballa M, Omil F, Lema J M, *How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters?* Rev Environ Sci Biotechnol 7 **(2008)** 125–138.

Tetreault G R, Bennett C J, Shires K, Knight B, Servos M R, McMaster M E*, Intersex and reproductive impairment of wild fish exposed to multiple municipal wastewater discharges*, Aquat. Toxicol. 104 (**2011**) 278– 290.

Teychene B, Guigui C, Cabassud C, *Engineering of an MBR supernatant fouling layer by fine particles addition: A possible way to control cake compressibility,* Water Res. 45 (**2011**) 2060 -2072.

Tomaszewska M, Mozia S*, Removal of organic matter from water by PAC/UF system,* Water Res. 36 (**2002**) 4137–4143.

Torretta V, Urbini G, Raboni M, Copelli S, Viotti P, Luciano A, Mancini G*, Effect of Powdered Activated Carbon to Reduce Fouling in Membrane Bioreactors: A Sustainable Solution. Case Study*, *Sustainability 5* (**2013**)1501-1509.

US EPA*, Powdered Activated Carbon: Overview, http://iaspub.epa.gov/tdb/pages/treatment/treatmentOverview.do?treatmentProcessId=2109700949.*

Vigneswaran S, Chaudhary D S, Ngo H H, Shim W G, Moon H, *Application of a PAC-Membrane Hybrid System for Removal of Organics from Secondary Sewage Effluent: Experiments and Modelling, Sep. Sci. Technol. 38 (**2003**) 2183- 2199.*

Von Gunten U, *Review: Ozonation of drinking water: Part I. Oxidation kinetics and product formation,* Water Res. 37 (**2003a**) 1443-1467.

Von Gunten U, *Review: Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine,* Water Res. 37 (**2003b**) 1469-1487.

Wahlberg C, Björnelius B, Paxéus N, *Läkemedelsrester i Stockholms vattenmiljö. Förekomst, förebyggande åtgärder och rening av avloppsvatten. Läkemedel – förekomst i vattenmiljön, förebyggande åtgärder och möjliga reningsmetoder,* Stockholm Vatten AB (**2006**).

Wahlberg C, Björlenius B, Paxéus N, *Läkemedelsrester i Stockholms vattenmiljö - Förekomst, förebyggande åtgärder och rening av avloppsvatten,* ISBN 978-91-633-6642-0, Stockholm Vatten AB (**2010**).

Westerhoff P, Yoon Y, Snyder S, Wert E, *Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes,* Environ. Sci. Technol., 39 (**2005)** 6649-6663.

WHO 2014. Antimicrobial resistance: global report on surveillance. World Health Organization, Geneva, Switzerland, ISBN 978 92 4 156474 8, WHO (**2014**).

Yamashita T, Yamamoto-Ikemoto R, *Nitrogen and Phosphorus Removal from Wastewater Treatment Plant Effluent via Bacterial Sulfate Reduction in an Anoxic Bioreactor Packed with Wood and Iron,* Int. J. Environ. Res. Public Health 11 (**2014**) 9835-9853.

Yu Z, Peldszus S, Huck P M, *Adsorption characteristics of selected pharmaceuticals and an endocrine disrupting compound—Naproxen, carbamazepine and nonylphenol—on activated carbon,* Water Res. 42 (**2008**) 2873 – 2882.