Isabel Johanne Eriksen

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Ways to remove phthalates in wastewater treatment processes to prevent environmental contamination.

Bachelor's thesis in BKJ
Supervisor: Alexandros Asimakopulos
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28.04.2023

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Abstract

While water covers most of the earth’s surface, only a small part of it is available for human activities.(1) That part only declines with our increasing population and the huge amount of waste produced annually. One of the main concerns around the world is the increasing demand for safe and accessible drinking water.(1) The importance of this cannot be understated, as poor water quality or contaminated water can put human health at risk.(1) For example, in China the concentration of DEP (diethyl phthalate), DBP (dibutyl phthalate), and DEHP (di-2-ethylhexyl phthalate) was limited below 0.3 mg/L, 0.003mg/L and 0.008 mg/L by the Hygienic Standard for Drinking Water in China. Thereby classifying them as priority pollutants in all of China.(2)

The best performing conventional wastewater treatment method is activated sludge (AS) with a removal rate of over 90% for all phthalate esters (PAEs) but had a lot lower values in some wastewater treatment plants (WWTPs).(3) The best overall method was found to be membrane filtration with a rate of 99.9% for both DEP and DEHP using reverse osmosis and nanofiltration (RO+NF). (3)

Introduction

The discharge of organic matter and other chemicals from urban, agricultural, and industrial areas often end up in various waterways and by extension in wastewater treatment plants (WWTPs) in many cases.(4) The effluent from WWTPs is regulated on a national level in order to limit the total load of different recipients as well as minimising potential problems in the receiving waters.(5) The different treatment methodologies used in conventional WWTPs can be roughly divided into 4 main groups; physical or mechanical treatment(5), chemical treatment, electrochemical treatment and biological treatment. (6) While some nanotechnology has demonstrated promising potential in removal endocrine disrupting chemical (EDCs) and by extension emerging micropollutants (EMPs) in WWTPs (6, 7) that is beyond the scope of this thesis.

Emerging micropollutants (EMPs) are defined as compounds that are synthetic or natural, they are released from point-/nonpoint resources and end up in an aquatic environment at a low concentration. These compounds are not frequently monitored and may have adverse effects on both marine environments and human health. These EMPs can come from pharmaceuticals, personal care products, industrial chemicals, and many others. Most

WWTPs are not designed to remove EMPs especially not at low concentrations, and this makes the treatment process vulnerable for leaks of pollutants(8).

Some of these can have potentially severe consequences for water quality and as well as marine life since they are endocrine disrupting chemicals (EDCs).(5) One group of chemicals namely phthalates, also called phthalate esters (PAEs), have become one of the most widespread classes of organic contaminants(4). They have been detected in many environmental media across the globe, like in air(9), water(10), sediments(11) and wastes(12). This bachelor thesis aims to reflect around and answer the following issue:

"Ways to remove phthalates in wastewater treatment processes to prevent environmental contamination."

Some of these PAEs are not as soluble in water and is found in higher concentration in sludge. Especially higher molecular weight PAEs like DEHP and DNOP, accumulate easier in organic solids(13). Phthalates can enter the environment in more complex ways like through waste (14) and sediments(12) that will not be discussed. Their metabolites will also not be discussed in detail in this paper.

Theory

How is a WWTP build up

Wastewater treatment plants (WWTPs) typically employ primary (sometimes also called pretreatment), secondary and a tertiary treatment process (figure 1) (3). The main goal of primary treatment is to remove as much solid material from the system as possible and be cheap as well as fast.(15) One common choice is sedimentation or coagulation.(15) Secondary treatment techniques involve some sort of chemical or microbial process performed on the water from primary treatment.(15) These can vary from activated sludge (AS) to membrane bioreactor (MBR).(15) A bioreactor are systems (or devices) that provide a biologically active environment and these micro-organisms are unable to move.(16) Tertiary treatment aims to further remove microbes and other substances with the help processes like UV and chlorine disinfection, but also other methods as seen in figure 1.(15)

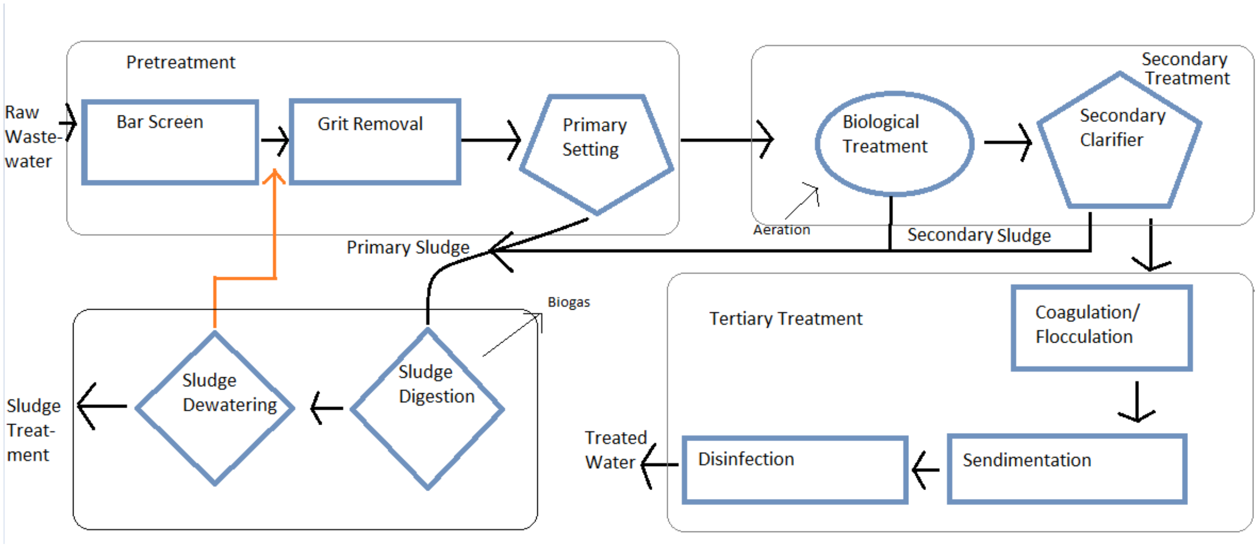

Figure 1: How a typical conventional WWTP is build up. Adaped by (3)

Conventional treatment processes

Activated sludge (AS) is a biological process where oxygen is added to sewage.(17) This sewage is already rich in naturally occurring oxygen and by agitating the sewage in this environment it gains the essential conditions for growth of small bacteria and organisms after settling.(17) It is at this point the sewage is called AS.(17) When added to raw sewage it oxidizes the organic solids and separates solids dissolved in the sewage.(17) In this AS system both raw sewage and AS are added into an aeration tank and left there until completely settled.(17) Afterwards the sludge is removed from the tank leaving behind the effluent for possible further treatment.(17) Following this process, the once settled sludge can be reactivated before re-entering the tank for reuse or be further processed as seen in figure 1.(17)

Oxidation ponds (OP), also called waste stabilization ponds, are large, shallow basins where raw sewage is treated only by processes involving algae and bacteria.(18) OP are used for sewage treatment in tropical and temperate climates(18) and their low energy consuming ecosystems makes them attractive in more rural areas.(19) There are two main types of OP, facultative ponds and anaerobic ponds.(18) Facultative ponds can be further split into two types, primary facultative ponds that receive raw sewage and secondary facultative ponds that receive wastewater free of particles.(18) Anaerobic ponds receive wastewater with high organic content.(18)

Tricking filter (TF) a method consisting of a fixed bed of rocks, gravel, porous materials, etc that is covered in slime.(20) Wastewater or sewage flows downward on this biological slime layer, this layer has an aerobic and an anaerobic sub layer.(20) If the filter is not porous then additional care is needed to sustain the slime layer.(20) The aerobic conditions can be maintained by splashing or force airflow through the bed if the natural convection of air is not enough.(20) This method involves both absorption and adsorption of organic compounds with the help of microbial slime.(20) The dissolved air in wastewater provides enough oxygen to fuel the biochemical oxidation of organic compounds.(20) Over time the slime layer grows, and an anaerobic layer is formed, in this layer decomposition takes place.(20) In short, TF removes organic solids by aerobic oxidation, anaerobic digestion, biosorption and coagulation.(20)

Coagulation/Flocculation

Coagulation/Flocculation (CF) is often a part of conventional tertiary treatment and is commonly used together with other methods like sand filtration in WWTPs to treat secondary effluent.(3) Flocculation means that smaller particles agglomerate into larger particles that can then be removed by sedimentation with the use of gravity.(21) It often uses multiple basins with different speeds in a row to promote interparticle collisions, all in order to produce a large floc for sedimentation.(21) A chemical helping with this process is called a flocculant.(15) Coagulation is an operation that removes particles in the colloid range of 1 nm- 1 µm.(15) The main goal is to destabilise colloidal particles, with the help of a coagulant they can promote collisions, ending in cohesion of particles.(15) These can be filtered out(3) or left to sediment.(15)

Adsorption, membrane, and filtration

Physical treatment (or mechanical treatment) can be divided into adsorption, membrane & filtration technologies. Adsorption is the most prevalent physical process due to its effective and reliableness. It is commonly considered one of the best techniques in wastewater treatment. That is due to its simplicity in regards of operation, flexibility of use and the lack of harmful by-products. The adsorption process is known as the most economical among the different methods. This is because other processes can cost more because of their difficulties of operation and/or high maintenance costs during operation periods.(6) Zeolites, mineral matter, activated carbon (AC), carbon nanotubes and biochar to name some, are the different types of adsorbents used to specifically remove EDCs. For phthalates has AC demonstrated up to 99% removal efficiency for DEP.(6) For AC both powdered activated carbon (PAC) and granular activated carbon (GAC) are both widely applied in WWTPs.(22)

Membrane technologies are considered another promising physical method. Some of the advantages with the membrane treatment process are as follow, a broad spectrum of selectivity, no formation of by-products or metabolites, continuous operation, and high adaptability to many different conventional water treatments. The generated effluent is often of high quality with a low concentration of organic chemicals and the method is considered as an excellent alternative to adsorption.(6)

Micro-membrane filtration (MF) employs membranes with pore sizes in the 0.05-10 µm range and is commonly made from some sort of polymer.(23) Ultrafiltration (UF) has pores sizes in the range of 0.001-0.05 µm in their membrane.(23) UF and MF membranes are porous, but UF membranes almost always have an asymmetric structure and typically operates with low pressure like 2-5 bar, but can vary from WWTP to WWTP. (23) MF membranes can vary in structure from symmetrical and uniform to very asymmetrical.(24) Similar to UF, MF also normally operates with low pressure.(24) Nanofiltration (NF) has pores smaller than that of UF, ranging from 1 to 10 nm, but unlike UF the process is driven by higher pressure and the membrane is often charged.(25) The pore sizes are slightly bigger than in reverse osmosis (RO).(25) Reverse osmosis (RO) have reverse osmosis membranes that allow water to pass through while hindering other solutes like salt or low molecular weight molecules.(26) RO is driven by the liquid in this membrane process. (26)

Chlorination

Chlorination involves using chlorine (or chlorine containing compounds) to inactivate/destroy pathogens and other substances present in the water. Chlorination was a wide success and is used to disinfect water across the world. However, in wastewater treatment it is highly desirable that the final effluent released to the environment is free of any harmful substances. As chlorination is the final step in the process as seen in figure 1, the existence of harmful chemicals and chlorine residuals can lead to them undergoing unwanted chemical transformations.(6)

Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) are regarded to be effective in the reduction of micropollutants.(3) These methods work by forming hydroxyl radicals either as a direct or indirect result depending on the exact method, and using them to promote oxidation of compounds. Since hydroxyl radicals has a strong oxidation capacity many compounds ends up converted to CO_2, inorganic ions and water.(2)

The photo-fenton system is used for pretreatment of wastewater before it enters a bioreactor for further treatment.(27) This coupled photo-fenton-biological system uses a light source that mainly emitting light at a wavelength of 254 nm and an added catalyst.(27) This is commonly an iron-based substance like $FeCl_3$ but can also be H_2O_2.(27) The Fe^{+3} or some added H_2O_2 is responsible for the generation of hydroxyl radicals, they carry out the oxidation of compounds found in wastewater.(27)

Ozonation uses ozone as an oxidizing agent and can react with many organic and inorganic compounds.(28) Ozone reacts with solutes either via direct oxidation, where the O_3 attack takes place on an electron-rich site of a solute, or an indirect reaction by making OH radicals.(28) The OH radicals are formed as the result from a decomposition of O_3.(28) Ozone reactions are often chain reactions, and direct reactions have been found to be highly selective with solutes containing double bonds.(28) The initiation of ozone decomposition can be enhanced by adding H_2O_2 or increasing the pH.(28)

The ultraviolet (UV)/H_2O_2 oxidation process directly generates hydroxyl radicals and have been found to reduce the amount of endocrine disrupting chemicals in wastewater quite effectively. (28) The wavelength commonly used is just above 250 nm, as nitrate ions effectively absorb UV light below 250 nm.(28) The result ends with NO_2^- that might interfere with the oxidation reaction.(28)

Membrane bioreactor and moving bed biofilm reactor

Membrane bioreactor (MBR) consists of a combination of activated sludge (AS) and membrane separation process.(3) Membrane separation process makes use of membrane filtration to separate solids and micro-organisms from the water.(3) In MBR the types of membranes, MF, UF, or NF take on the role of secondary clarifier seen in conventional activated sludge. (3)

Moving bed biofilm reactor (MBBR) is based on attached growth of biofilm on carriers. (29) These carriers are suspended into the reactor and with suspended activated sludge on these carriers, they work to break down organic matter in the influent water.(29)

Phthalates

Phthalate esters (PAEs) seen in figure 2 are plasticizers that increase the plasticity of industrial polymers like polyvinyl chloride (PVC).(4, 30) They are used in food handling, storage and in products like rubber and many other consumer products. (30) They are not chemically bound to the polymers however and exist in a freely leachable phase. The PAEs can leach, evaporate, or migrate into the environment by entering the waterways.(4, 30) Some PAEs like DEP, DBP and DEHP as seen in figure 3, are classified as toxic compounds to humans and wildlife alike.(31)

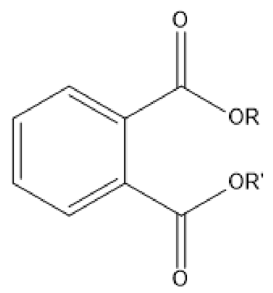

Figure 2: general structure of phthalates, adapted from reference (30)

In this thesis the focus is on di(2-ethylexyl) phthalate (DEHP), benzyl butyl phthalate (BBP), di-n-butyl phthalate (DBP), diethyl phthalate (DEP), dimethyl phthalate (DMP) and di-n-octyl phthalate (DNOP).(5) In industry, a lot of the phthalates used are high-molecular-weight phthalates (HMWPs). HMWPs are defined as compounds in which the alcohol side chain has five or more carbon atoms. DEHP and DNOP are the only HMWPs in this thesis.(32)

Low-molecular-weight phthalates (LMWPs) on the other hand, are compounds that contains one to four carbon atoms in the alcohol side chain. That means the rest of the PAEs, like DMP, DEP, BBP and DBP are LMWPs.(32) Of the six different phthalates seen in figure 3, all of them are on lists of priority pollutants by the European Union. DBP, BBP and DEHP are also on the United States Environmental Protection Agency's priority list of hazardous substances.(32) Phthalates are also considered to be endocrine disrupting chemicals (EDCs).(33)

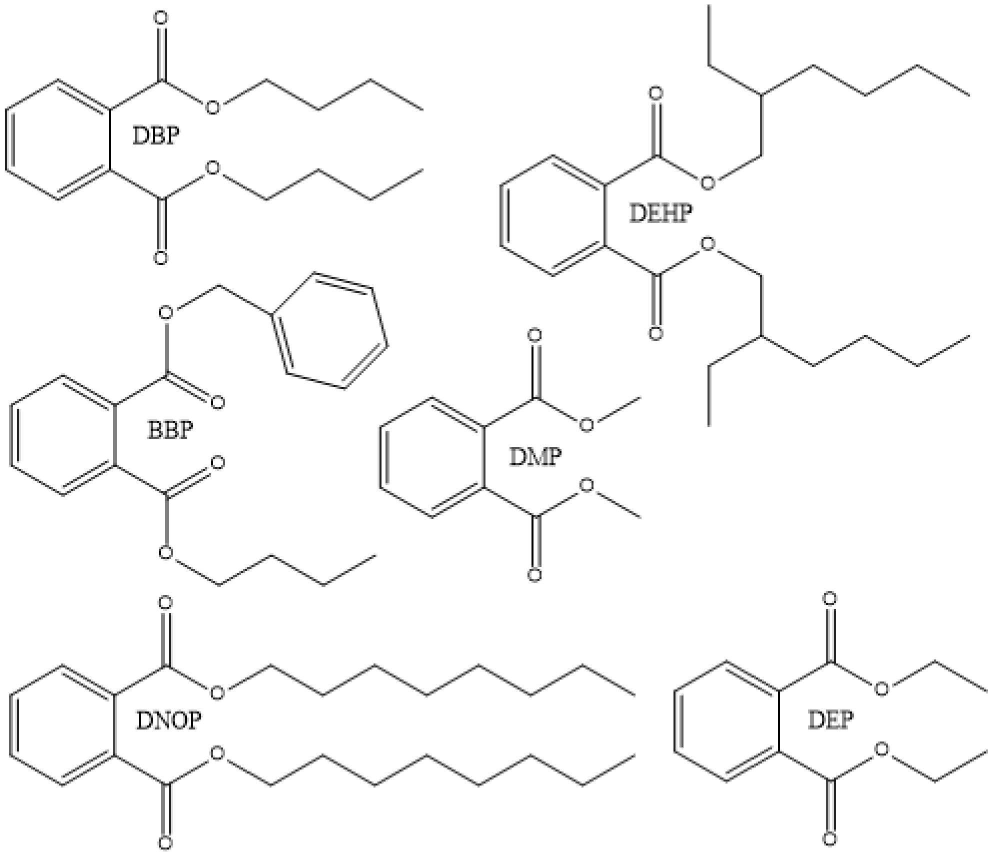

Figure 3: The various phthalates that are the main focus of this thesis, adapted from (30).

Endocrine disrupting chemicals are substances and compound mixtures that can alter normal hormone functions. The endocrine system is effected even at low concentrations.(6) The effect of EDCs on rodents have shown that DBP, DEHP, BBP are oestrogenic and have adverse reproductive effects. (4, 31) Some of these PAEs have been identified in human urine and amniotic fluid as well. It was also concluded in those studies that humans were not likely to be more sensitive than rodents to the effects of PAEs, and may even be less sensitive.(34)

Perinatal exposure of PAEs, specially DBP and DEHP might also disrupt or impact human Leydig cell development and lead to incomplete development of male characteristics.(35) Leydig cells are the testicular cells responsible for biosynthesis of and secretion of androgens. They are critical for the development of normal reproductive function in males.(36)

Discussion

Conventional WWTPs

Table 1 summarizes data of the six selected PAEs in WWTPs from different countries. As can be seen from the table, both influent and effluent concentrations of our PAEs show significant variations. DBP had the highest concentration of 2497 μg/L in influent wastewater for WWTP at Alice in Eastern Cape, South Africa (19). Also, in the northern WWTP of China, DBP was the most abundant with a concentration up to 21.01 μg/L.(37) DEHP, however had the highest level of our PAEs in other countries (38). In Alice, South Africa, had an influent concentration of up to 96.18 μg/L.(19) A similar phenomenon also appeared in Denmark WWTPs, and the highest concentration was 84.10 μg/L.(39) The high levels of DEHP might be explained by the wide consumption of polyvinyl chloride (PVC).(40) There have been a large variation in both distribution and concentration of PAEs among the different areas. Which may be from different receiving sources of wastewater to WWTPs. One WWTP might receive wastewater mainly from a relatively single source like domestic wastewater. Others may get wastewater from various sources like, domestic wastewater, industrial wastewater, agricultural run-off, and street run-offs.

The most common method used was activated sludge (AS) with other methods like oxidation pond (OP) and tricking filters (TF) used in some WWTPs. Table 1 reveals that the removal rate of the six PAEs varies from 14.20% to 99.82% in those selected WWTPs. DBP has the highest overall removal efficiency of all PAEs, and BBP has a removal rate of over 80% in many cases. The other four PAEs have a lower removal efficiency of only about 70% in most cases. AS effectively eliminated, many of our PAEs, and their max removal rate were 99.82 (DMP), 90.60% (DEP), 99.47% (DBP), 91.73% (BBP), 94.00% (DEHP), and 95.55% (DNOP). When compared with the max removal rate of PAEs by OP at just 61.24% (DMP), 82.05% (DEP), 98.34% (DBP), 95.9% (BBP), 76.75% (DEHP), and 79.02% (DNOP), respectively, which were lower than the values produced by AS for the most part. TF did better than OP with some of these removal rates of PAEs at 76.59% (DMP), 75.62% (DEP), 98.46% (DBP), 88.02% (BBP), 82.13% (DEHP) and 88.63% (DNOP). While TF did better than OP with HMWPs, AS still did better than them both. When comparing LMWPs OP and TF were more even, with DMP having a better rate using TF than OP, and the opposite applying for DEP. Still, AS got the best overall removal rate for these PAEs compared to OP and TF.

For AS the main advantage is a medium to high removal efficiency, and a lower capital/operational cost than other methods. However, this method produces a large amount of contaminant enriched sludge that also needs to continue treatment. Another disadvantage is that it's not fully effective in the elimination of some PAEs, especially those with high hydrophilicity.

Table 1: concentration range detected of the six PAEs in wastewater (µg/L) and their removal rate, process and country. ND, Not Detected; the locations are as follows: A1, Adelaide; A2, Alice; A3, Seymour; B1, Alice; B2, Bedford; B3, Berlin

PAEs	**Processes**	**Influent**	**Effluent**	**Removal (%)**	**Country**	**Reference**
DMP	AS	0.269-4.31	ND-0.237	93.88	Denmark	(39)
	AS	0.82±1.13	ND	90	France	(41)
	OP	42.1±0.03	17.0±0.4	59.6	Nigeria	(42)
	AS	23.4±0.2	12.3±0.2	26.9	Nigeria	(43)
	AS	1.96	ND	99.82	China	(37)
	AS.[A1]	1.35-12.07	0.62-2.37	72.16	South Africa	(44)
	AS.[A2]	1.14-23.14	0.64-4.57	77.66	South Africa	(44)
	AS.[A3]	ND-6.33	ND-4.10	27.21	South Africa	(44)
	AS.[B1]	0.89-24.51	0.34-4.87	79.38	South Africa	(19)
	OP.[B2]	2.27-11.74	0.53-5.15	61.24	South Africa	(19)
	TF.[B3]	1.12-5.52	0.53-2.02	76.59	South Africa	(19)
DEP	AS	7.71±5.52	0.78±0.22	90	France	(41)
	OP	12.9±0.1	11.1±0.1	36.2	Nigeria	(42)
	AS	21.1±0.9	10.2±0.1	52.3	Nigeria	(42)
	AS	4.56	0.43	90.60	China	(37)
	AS.[A1]	2.53-24.42	0.17-8.89	73.56	South Africa	(44)
	AS.[A2]	2.20-25.72	0.12-5.97	80.63	South Africa	(44)
	AS.[A3]	1.12-13.83	ND-7.32	32.97	South Africa	(44)
	AS.[B1]	2.29-27.19	0.40-7.32	76.99	South Africa	(19)
	OP.[B2]	4.02-35.29	1.02-6.74	82.05	South Africa	(19)
	TF.[B3]	2.15-15.32	0.91-3.78	75.62	South Africa	(19)
DBP	AS	15.34-24.67	1.83-2.73	88.39	Denmark	(39)
	AS	1.10±0.37	0.15±0.12	86	France	(41)
	OP	21.9±0.8	18.1±0.02	28.2	Nigeria	(42)

	AS	29.9±0.7	18.1±0.02	29.3	Nigeria	(42)
	AS	21.01	2.08	90.10	China	(37)
	AS.[A1]	ND-451.48	ND-26.47	95.45	South Africa	(44)
	AS.[A2]	3.05-2488.31	1.17-22.34	99.47	South Africa	(44)
	AS.[A3]	2.70-277.89	1.05-7.68	93.74	South Africa	(44)
	AS.[B1]	3.12-2497	1.23-24.19	99.41	South Africa	(19)
	OP.[B2]	6.92-1494	3.36-22.08	98.34	South Africa	(19)
	TF.[B3]	1.59-791	2.77-6.25	98.46	South Africa	(19)
BBP	AS	9.41-80.74	1.99-4.33	91.73	Denmark	(39)
	AS	1.12±0.54	0.30±0.12	73	France	(41)
	OP	9.93±0.1	0.40±0.1	95.9	Nigeria	(42)
	AS	13.1±0.9	3.34±0.11	72.8	Nigeria	(42)
	AS.[A1]	2.38-80.70	ND-13.73	84.87	South Africa	(44)
	AS.[A2]	ND-52.12	0.75-8.75	86.23	South Africa	(44)
	AS.[A3]	1.73-14.32	0.76-13.84	42.58	South Africa	(44)
	AS.[B1]	ND-52.25	0.28-8.95	86.54	South Africa	(19)
	OP.[B2]	5.09-71.62	ND-15.84	88.79	South Africa	(19)
	TF.[B3]	6.32-36.42	ND-4.39	88.02	South Africa	(19)
DEHP	AS	53.23-84.10	2.08-9.93	93.16	Denmark	(39)
	AS	22.46±13.22	5.02±1.53	78	France	(41)
	OP	45.2±0.6	37.4±0.2	14.2	Nigeria	(42)
	AS	34.1±0.01	16.9±0.0	61.5	Nigeria	(42)
	AS.[A1]	3.44-48.16	2.05-18.25	67.98	South Africa	(44)
	AS.[A2]	6.13-94.87	1.73-14.82	83.94	South Africa	(44)
	AS.[A3]	2.68-62.60	2.42-24.91	35.96	South Africa	(44)
	AS.[B1]	6.16-96.18	1.84-15.13	83.62	South Africa	(19)
	OP.[B2]	21.36-85.04	1.47-30.99	76.75	South Africa	(19)
	TF.[B3]	8.80-27.89	1.54-5.64	82.13	South Africa	(19)
DNOP	AS	0.10±0.16	ND	79	France	(41)
	AS	9.63	5.28	45.13	China	(37)
	AS.[A1]	ND-21.75	ND-4.15	75.06	South Africa	(44)
	AS.[A2]	3.06-63.59	ND-6.02	89.81	South Africa	(44)

AS.[A3]	ND-12.26	ND-7.57	34.22	South Africa	(44)
AS.[B1]	3.08-67.37	ND-5.78	95.55	South Africa	(19)
OP.[B2]	3.11-42.48	ND-12.88	79.02	South Africa	(19)
TF.[B3]	3.74-11.55	ND-4.69	88.63	South Africa	(19)

Advanced wastewater treatment

Coagulation/flocculation (CF) does not have a lot of available literature on PAE removal. Furthermore, that limited literature shows poor performance in the elimination of PAEs as seen in table 2. Matamoros and Salvadó (45), found the removal efficiency of CF to only be 3-6% for DMP. Luo et al.(38) got slightly better values for DMP at a 19% removal rate. They also studied DEHP, that had a 70% removal rate. Indicating that HMWPs with their higher hydrophobicity might have better results in CF, however Melo-Guimarães et al. (46) only got a 3% removal rate for DEHP so the results depend heavily on both coagulant and dosage. That is information that these studies often either neglect to mention partially or fully, leaving only the removal rate as an indication. Also, Huang et al.(37) reported that coagulation-air flotation (plus filtration) of PAEs from secondary effluent was infeasible to remove them from the solution. Further supporting CF as a less than optimal method with current available literature.

Table 2: The removals of DMP and DEHP by CF. NM: Not Mentioned

Coagulant	**Dosage**	**PAEs**	**Removal (%)**	**References**
$FeCl_3$	100, 200 mg/L	DEHP	70	(38)
NM	NM	DMP	19	(38)
NM	NM	DMP	3-6	(45)
Zetag 8140	NM	DEHP	3	(46)

Activated carbon (AC) has demonstrated to be more efficient than other methods to eliminate traces of organic compounds in the secondary effluent. Due to its large surface area and chemical nature, AC, as seen in Table 3, is clearly superior to CF in elimination of PAEs. Both powdered AC (PAC) and granular AC (GAC) are widely applied, and has removal efficiencies ranges from 50 to 100%, among which the higher removal ratios were generally seen for bigger compounds. Gani et al.(47) reported that 100% of DEHP was eliminated with

PAC, compared to 60% of DEP and 88.46% of DBP using the same method. The higher rate of reduction was likely associated with its more hydrophobic character due to longer carbon chains.(22) GAC was also employed as adsorbents, in part due to its surface functional groups consisting of doped carbon with Fe/S. M. Pu et al.(48) found the removal rate of DEHP to reach up to 98% using GAC. The main disadvantage with AC is regeneration and that makes it more costly to implement in a WWTP.

Table 3: The removals of some PAEs by AC

Adsorbent	**Dosage**	**PAEs**	**Removal (%)**	**References**
PAC	1-10 mg/L	DEP	60	(22)
	1-10 mg/L	DBP	88.46	(22)
	1-10 mg/L	DEHP	100	(22)
	15 mg/L	DEHP	69	(49)
	10 mg/L	DEHP	100	(47)
GAC	1 g/L	DEP	98	(48)

Advanced oxidation processes (AOPs) including photo-fenton, ozonation, and ultraviolet (UV) radiations are generally regarded as good alternatives due to their rapid degeneration rates.(28) In table 4 the different methods are shown and their removal efficiency. They are comparably effective for PAE removal in some cases, while not as effective as AC, this method is still better than CF overall. The generation of hydroxyl radicals that these processes depend on convert PAEs to mainly CO_2, inorganic ions, and water if the reaction runs completely. Some of these reaction by-products can however endanger the lifes of marine organisms, and some were found to be skin irritants or corrosive to human skin.(3) This is a serious disadvantage for AOPs, the generation of oxidation by-products some of which are more toxic than the original pollutants. Of the AOPs, ozonation tend to yield better results than UV, both when a single technique is applied and with the addition of H_2O_2 depending on the concentration added. Chlorination did not give a high removal rate compared with other AOPs and used the longest time of the methods listed in table 4. High costs in energy, operation, and maintenance(3) also makes AOPs less favourable when compared to AC. The possible formation of toxic by-products means that careful consideration needs to be taken in removing one certain PAE by AOPs.

Table 4: The removals of DEP and DEHP by different AOPs

Treatment process	**PAEs**	**Removal (%)**	**References**
O_3 (9mg/L):5 min	DEP	80	(28)
UV_{254}: 2 min	DEP	50.3	(28)
O_3 (5 mg/L)+H_2O_2 (10, 30, 50 mg/L):2 min	DEP	70-80	(28)
UV_{254} + H_2O_2 (10, 30, 50 mg/L): 2 min	DEP	53-92.2	(28)
UV_{254} + chlorination (3 mg/L):60-120 min	DEP	40	(45)
Photo-Fenton$_{254}$ + H_2O_2 (4 mM/L): 60 min	DEHP	71.6±1.2	(27)
Photo-Fenton$_{254}$ + Fe^{3+}(3 mM/L): 60 min	DEHP	71.8±1.6	(27)

Membrane filtration typically incorporate microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Table 5 shows some PAEs and their removal rate with different membrane filtration methods. From table 5, the removal rate follows the order: NF+RO>RO>NF>UF. UF likely has poor elimination of PAEs due to the membrane pore sizes, they are too large compared with the molecular sizes of PAEs. PAEs are still removed however, that happens either via adsorption on to membrane polymers or some interaction with organic matter that are present.

A high PAEs removal rate, ranging from 82.3% to 99.9% (often >90%) for NF and RO is due to their smaller pores. They also show a better removal efficiency for HMWPs than LMWPs, which is likely due to their differing properties. While RO is highly effective there is still a small part of PAEs left in the treated water. Hence, RO needs a complementary process to eliminate all PAEs. Ozay et al.(50) got removal rates of 99.9% for DEP and DEHP by combining NF and RO, and thereby nearly removing all PAEs from the water. This method is also applicable for inorganic compounds. The disadvantage is to membrane filtration is membrane fouling and high energy consumption. There is also the concentrated residual to handle after the filtration process to consider.

Table 5: Removals of some PAEs by membrane filtration.

Membrane	**PAEs**	**Removal (%)**	**References**
UF	DEP	99.9	(51)
	DBP	89.7	(51)
	DEHP	79	(46)
	DEHP	99.6	(51)
NF	DEP	99.9	(51)
	DBP	99.9	(51)
	DEHP	99.9	(51)
	DMP	82.3	(52)
	DEP	86.7	(52)
	DBP	91.5	(52)
	DEHP	95.4	(52)
	DNOP	95.1	(52)
	DEP	97.7	(50)
	DEHP	99.9	(50)
RO	DEP	95.1	(51)
	DBP	95.1	(51)
	DEHP	99.9	(51)
NF+RO	DEP	99.9	(50)
	DEHP	99.9	(50)

Table 6 has some data on the removal efficiency of PAEs by membrane bioreactor (MBR). Most of the research found removal of PAEs in the range of 75-96% by MBRs. There were some poor removal rates (27.8-29%), that were likely a consequence of operation parameters and pore sizes selected for the membrane like how UF and NF differed. The effective elimination of most PAEs comes at a cost however, high energy consumption, membrane fouling and aeration cost in addition to the funds need for installation, makes this method a bit costly for WWTPs. (3) But if the parameters and appropriate membranes are chosen, this method can be a good fit, especially with another method to further improve the removal efficiency in WWTPs.

Table 6: Removals of selected PAEs by MBR and MBBR

System	**Water type**	**PAEs**	**Removal**	**References**
MBR	Syntentic Wastewater	DEHP	29	(53)
	WWTP effluent	DEHP	27.8	(54)
	WWTP effluent	DEHP	75	(46)
	Municipal solid waste leachate	DMP	78	(55)
	Municipal solid waste leachate	DEP	81	(55)
	Municipal solid waste leachate	BBP	77	(55)
	Municipal solid waste leachate	DEHP	96	(55)
	Municipal solid waste leachate	DNOP	82	(55)
MBBR	Synthetic wastewater	DEP	84.04-94.87	(29)

Moving bed biofilm reactor (MBBR) can improve the removal of PAEs by adding suspended AS along with biofilm growth on the carriers into the reactor. MBBR has a high and stable PAE removal rate at 84.04-94.87% for DEP, and there is no sludge bulking. It also only needs simple maintenance, is simple to operate, high specific biomass activity, and has plentiful microbial species.(29) The disadvantage to this method is high aeration cost and carriers blocking. Still, MBBR is a preferable option for removing PAEs when compared to some of the other methods.

Conclusion

In this thesis different methods used to eliminate our six PAEs have been investigated. DEHP had the highest concentration in most locations and DBP had the highest values in the others. AS did get a removal rate over 90% for all PAEs, but also as low as 29.3% for DBP in one WWTP. Of the conventional treatment processes AS achieved better results than OP and TF but also the biggest difference in reported numbers. Thus, advanced treatment processes are needed to better remove these compounds. AC, AOPs, membrane filtration, MBR and MBBR all had overall better performance than AS, but also accompanied with some deficiencies like toxic by-products, regeneration, high operational cost, etc. CF was the only one of the advanced processes to perform worse than AS and had the worst removal rate reported of all processes. On the other hand, the best performing method was membrane filtration, especially RO+NF with a removal rate of 99.9% for both DEP and DEHP. All these methods fall into one of the main categories, pretreatment, secondary treatment, and tertiary treatment. By using different methods combined it is likely able to achieve an even better removal rate. However, further research is needed in order assess which combination of processes achieves this, since most simply focus on one or a few methods in isolation.

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