MICROPOLLUTANT REMOVAL FROM WASTE WATER TREATMENT PLANT- A REVIEW
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ABSTRACT
Through improved methods of chemical analysis, micropolllutants, such as pharmaceuticals and endocrine disrupting compounds are increasingly being detected in our water bodies. In these cases these enter the wastewater after being excreted in urine and faeces. In the sewage plant, a part of the substances is eliminated via sorption and biological degradation. The rest is discharged with the treated effluent. In surface water and during bank infiltration further elimination is observed but some micropolllutants persist, acting as wastewater tracer in groundwater and are also detected in drinking water. This article describes possible measures for eliminating trace organsics in waste and drinking water treatment. These include on the one hand, permanent measures at the source such as an ecolabel for pharmaceuticals and personal care products as well as the separate treatment of strongly polluted wastewater, e.g. in hospital or industry. However, as most of these measures can only be implemented over the long term, it is expedient on the other hand, to also consider technical measures such as increasing the sludge age in the activated sludge tanks of WWTP and for crucial locations, additional treatment with activated carbon.

KEYWORDS: Activated Carbon, Adsorption, Micro-pollutants, Pharmaceuticals, Wastewater.

INTRODUCTION
The conventional notation for low concentration substances that are not naturally present in the environment is micropolllutants. Around 100,000 chemicals are registered in the European Union and are, as a result of manufacturing, disposal and use, emitted to the environment. A substantial proportion of the total load of micropolllutants enters the receiving waters by discharge from urban areas. The major discharge points are direct industrial discharges (with or without treatment), wastewater treatment plants (WWTPs), separate storm sewers, combined sewer overflow (CSOs), and building drains and smaller discharge pipes and surface runoff. The primary sources of micropolllutants are the products which contain them, such as household chemicals, personal care products, pesticides, vehicles, construction materials and road surfaces etc, as well as the chemicals used in manufacturing.

The discharge concentrations of most micropolllutants are usually far below acute human toxic levels, and it is mainly adverse long-term effects and the ecological impact that is of concern. It has been established that some micropolllutants have hormonal or endocrine disrupting potential and current studies report that specific xenobiotic organic compounds (XOCs) in the effluents of wastewater treatment plants (and consequently also in storm water discharges, via CSOs) are responsible for effects such as sterile fish in certain recipients and on human.

Nonylphenol (from e.g. car wash detergents) is an example of an endocrine disrupting chemical that has been found in storm water. Else, traditional storm water micropolllutants are often divided into heavy metals (toxic to plants and animals), polycyclic aromatic hydrocarbons (PAHs) (carcinogenic) and herbicides/pesticides. It is noticed that the list of interesting storm water pollutants will need to be expanded in the future with the implementation of the Water Framework Directive (WFD). They therefore developed a methodology where “other miscellaneous organic compounds” (i.e. XOCs) were identified as well.

Water supply, urban drainage and wastewater treatment systems were originally designed to solve conventional problems (supply of potable water, flood protection and sanitation) and water quality research has mainly focused on organic matter and nutrients. The legislative requirement to achieve a reduction and/or elimination in the discharge of also some micropolllutants within the extremely short time frame of 20 years, as set out in the WFD has therefore placed the water authorities and utilities responsible for the treatment and disposal of wastewater and storm water, as well as industries which use and emit micropolllutants under enormous pressure. [Erik Lindblom, 2009]

METHODS
1. Activated carbon
Activated carbon is a material used to filter harmful chemicals from polluted water. It looks like tiny granules of black sand. As polluted water or air flows through an activated carbon filter, chemicals sorb or stick to the surface and within the pores of the granules. Most tap water filters and fish tank filters at home contain activated carbon and work the same way. Activated carbon filters are often used as part of a pump and treat system to clean up polluted groundwater. [EPA, 2001]

Activated carbon filters are also used to remove unwanted tastes, odours, radon, and some man-made volatile organic contaminants from drinking water. The efficiency of the unit depends on the type of activated carbon installed, the filter bed depth, the type of contaminants in the water and their concentration, and the contact time between the water and the carbon filter. Activated carbon filters do not adsorb every type of contaminant equally well. Carbon filters are easy to install and maintain, and operating costs are usually limited to filter replacement. Depending on the type and concentration of the contaminant being removed, some carbon filters may require special hazardous waste handling and disposal, which can be costly. Other filter types are available including charcoal and ceramic materials that treat the water similarly, through the adsorption of the contaminant onto the filter. The solid material used in an activated carbon filter is a specialized carbon manufactured for these purposes. Contaminants adhere to the surface of these carbon granules or become trapped in the small pores of the activated carbon. Generally, an activated
carbon filter is used with a pre-treatment filter to remove sediment or iron particles that may be present and can clog the carbon filter. Granular activated carbon, (GAC); treatment is most common for private water systems. Granular activated carbon is an effective filter for removing organic chemicals that may be in drinking water. Many other small devices use carbon that has been pressed into a solid block. Use of block carbon may result in a significant drop in home water pressure. These devices also clog easily if the water is cloudy or turbid. A synthetic resin may be a substitute for carbon. Although activated carbon is efficient in removing a variety of organic chemicals, a specially formulated synthetic resin may be a better absorber for a specific contaminant. [University of Rhode Island, 2003]

Powdered activated carbon adsorption: effective, but slow. Treatment with powdered activated carbon (PAC) is in small-scale pilot plants. In this process, PAC (particle diameter 10 – 50 μm) is added to the wastewater. Thanks to the huge surface area (1000 m²/g) and other specific chemical properties (e.g. charge, arrangement of molecules), many substances adsorb onto the particles. Activated carbon adsorption is a highly promising method for the removal of numerous micropollutants elimination rates of more than 80 % are achieved for many (but not all) substances in treated wastewater with a dose of 10 –20 mg PAC per litre. [Christian Abegglen, Adriano Joss and Hansruedi Siegrist, 2009]

2. Membrane processes
Several membrane types and applications were evaluated for the removal of micropollutants from Industrial waste water at pilot and full scale, including microfiltration, ultra filtration, nanofiltration, reverse osmosis, electro dialysis reversal, membrane bioreactors and combinations of membranes in series. Microfiltration and ultrafiltration are generally not fully effective in removing organic contaminants as pore sizes vary from 100-1000 times larger than the micropollutants which can slip through the membranes. [R.Rangel-Mende, 2001]

Membrane technology is widely used to filter micro pollutants from water. Osmotic theory implies pure water will move across semi-permeable membrane into wastewater until the contaminant concentrations of both liquids are equal. However, if external pressure is exerted on the “contaminant” solution, water will flow in the reverse direction from concentrated solution to dilute solution, from wastewater to clean water. This phenomenon, known as reverse osmosis (RO), can separate clean water from contaminated water. [Alaska Dept, 2010]

These processes have the advantage of selectivity compared to other techniques. Membrane processes involve the flow of a permeate through a porous media induced by a driving force and also promote retention of particle contaminates. A membrane technique is divided into three types based on the applied driving force: pressure, concentration and electrical. The pressure gradient process can be subdivided into ultrafiltration, microfiltration, Nano filtration and reverse osmosis. Other membrane processes work according to the size of the suspended solids. Particles smaller than a certain size are allowed to pass through the membrane whilst the largest are retained. Technology has advanced in this field and new kinds of membranes have been developed, for instance chemically active membranes that enhance the separation process. An electric current can also be applied when a membrane is used to separate certain species from wastewater streams. This enhances the process as the transport of ions across the porous or permeable membrane becomes faster. Either cations or anions are allowed to pass the membrane whilst the species of opposite charge is restricted. This technique has been widely applied in desalination plants. Membrane processes can be used at the end of a series of separation processes to reduce the concentration of micropollutant. This technique has been proved to be very efficient; however, it involves higher operational and capital cost. [R.Rangel-Mende, 2001]

3. Chlorination
Chlorine dioxide is widely used for the disinfection of relatively high quality water, such as groundwater or treated surface water. Dosing of chlorine dioxide to the finished water will protect the drinking-water distribution system. From microbiological recontamination and fouling. In this case, ClO₂ residuals are often kept < 0.05 – 0.1 mg L⁻¹. In the USA, ClO₂ is rather used for the preoxidation of surface waters. Common ClO₂ dosages range from 1 to 1.4 mg L⁻¹. Furthermore, ClO₂ is used for the disinfection of wastewater. Compared to disinfection with chlorine, chlorine dioxide has several advantages: it is more effective than chlorine for the inactivation of protozoa, its biocidal properties are not influenced by pH, and it does not react with ammonia. Furthermore, chlorinated and brominated disinfection by-products are not formed under proper generation condition. Compared to ozone, chlorine dioxide is more stable in water and provides residuals, which are required for the protection of distribution systems. However, ozone is more effective for the inactivation of microorganisms. Used for preoxidation, chlorine dioxide can control taste and odor and oxidize iron and manganese. However, the application of ClO₂ is limited by the formation of chlorite, which is considered a blood poison. The USEPA standard of 1 mg L⁻¹ for chlorine limits chlorine dioxide dosages to approximately 1.4 mg L⁻¹.Chlorine dioxide can only be used for preoxidation in combination with other oxidants (e.g., chlorine) due to a more stringent chlorite standard of 0.2 mg L⁻¹.[ Marc Martin Huber,2004]

4. Ozonation
Ozone (O₃) is a relatively unstable molecule of oxygen, which readily gives up one atom of oxygen providing a powerful oxidising agent, toxic to most water borne organisms. It is an effective oxidant to inactivate harmful protozoa that from cysts. It also works well against almost all other pathogens. Ozonized water is produced by passing oxygen through ultraviolet light or a “cold” electrical discharge. To use it as a disinfectant, it must be created on site and added to the water; generally the transfer occurs through bubble contact. The use of ozone induces some advantages; among them, the production of relatively fewer dangerous by products and the absence of taste and odour produced by ozonation.
Nevertheless, it has been discovered that the ozonation is susceptible to produce a small amount of suspected carcinogen bromated (BrO₃⁻), even if small amounts of bromine (Br⁻) are present in raw water. Moreover, due to its instability in water, ozone does not persist, thus leaving no disinfectant agents for the water still to be purified on its way to the consumer. [Pierre Mandel, 2007]

**FUTURE METHODS**

1. **Direct photolysis**

Direct photolysis occurs due to the breakdown of a compound by the absorption of light. Indirect photolysis is caused when photosensitises, such as nitrate and dissolved organic matter, absorb light and generate reactive oxygenated radicals that subsequently degrade other compounds. Many pharmaceuticals are readily susceptible to photolytic transformation. APIs that do not absorb light above 290 nm are more resistant to direct photolysis with natural light. Lamps employed in the removal of micropollutants focus mainly on low and medium pressure mercury lamps. Low pressure mercury lamps characteristically generate light at 254 nm while medium pressure lamps emit their energy at multiple wavelengths. Using a 110W, 254 nm UV lamp at 313K and 0.5 g/L, a 70% conversion of 0.25 µm initial concentrations of ibuprofen, 26.34 % of diclofenac, 95.78 % and 87.75 % degradation of mefenamic acid was observed to undergo direct photolysis with a half-life of 33 h under direct noon sunlight in mid-October at 45°N latitude. Carbamazepine and clofibric acid have photodegradation half-life times of 100 d in winter at 50°N. Conversely sulfamethoxazole, diclofenac, ofloxacin and propranolol undergo faster degradation with half-lives of 2.4, 5.0, 10.6 and 16.8 days, respectively. In a different set of experiments, clofibric acid, diclofenac, fenoprofen, isopropylantipyrine, ketoprofen, phenytoin and triclosan were removed in a laboratory situation (> 96 %) by ultraviolet photolysis alone. A fundamental parameter that determines the rate of degradation for photolysis is the decadic molar absorption coefficient. The decadic molar extinction coefficient is a measure of the capacity of a compound to absorb light. Ibuprofen, diphenhydramine, phenazone, and phenytoin have decadic molar extinction coefficients of 256/M/cm, 388/M/cm, 8906/M/cm and phenytoin 1260/M/cm, respectively. As indicated by the decadic molar extinction coefficients, 27.4 % removal of 5 μm initial concentrations of ibuprofen, 26.34 % of diphenhydramine, 95.78 % and 87.75 % degradation for phenazone and phenytoin, respectively, was observed. The experiment was carried out using an 11W low pressure lamp producing monochromatic UV light at 254 nm in a 500 mL quartz reactor. The antibiotic metronidazole achieved only 6 % removal with a low-pressure and 12 % with a medium pressure mercury lamp after 5 min exposure. Metronidazole has a crucial absorption centred at about 310 nm, which can be readily excited by a medium pressure lamp. In contrast, low pressure lamps only emit light at 254 nm and as a result, the important absorption at 310 nm is missed. The adsorption-lamp emission mismatch consequently explains the low removal with UVC light. As such, direct photolysis on its own is not an effective for removing pharmaceuticals from wastewater. Alternatively, photolysis coupled with Fe (III) and H₂O₂ or TiO₂ can remove over 98 % of pharmaceuticals including estrogens. [A. M. Deegan; B. Shaik; K. Nolan; K. Urell; M. Oelgemöller; J. Tobin; A. Morrissey, 2001]

2. **Electrochemical treatment**

Electrochemistry is a relatively new method for the treatment of wastewater (Chen, 2004). The treatment of acetaminophen using anodic oxidation with a Borondoped diamond (BDD) electrode has been successful during small scale investigations. This process allows complete mineralization of the acetaminophen due to the generation of large concentrations of hydroxyl radicals by the electrode. The BDD electrode was efficient even at low concentrations. BDD has high thermal conductivity, wide band gap, high e- and whole mobility’s, high breakdown electric fields, hardness, optical transparency and chemical inertness (Chen, 2004). Ultrasonic irradiation has been considered as a means of removing estrogenic compounds from contaminated water. Hormones, for example, estradiol, estrone and ethinylestradiol, were examined in single component batch and flow through reactors using 0.6, 2 and 4 kW ultrasound sources. Results showed 80-90 % reduction in the hormones within a 40-60 min period. Further investigations in this area would be useful to determine the toxicity of breakdown products and to examine the feasibility of larger scale applications of the technology. Diamond anodes may produce OH Radicals with high current efficiency. This is dependent on the mass transport of organic compounds to the anode not being a limiting factor. [A. M. Deegan; B. Shaik; K. Nolan; K. Urell; M. Oelgemöller; J. Tobin; A. Morrissey, 2001]

3. **Fenton reactions**

Fenton chemistry involves reactions of hydrogen peroxide in the presence of iron to generate hydroxyl radicals. Ultraviolet light enhances this generation by the photo reduction of Fe (III) to Fe (II). Since iron is abundant and non-toxic, Fenton reactions are a viable option for wastewater treatment. Photo-Fenton reactions have been used for the degradation of diclofenac. Complete mineralisation of diclofenac and its intermediates via photo-Fenton reactions in a concentric photo reactor took approximately 50 min. Compound parabolic collectors have also been used to mineralize diclofenac in approximately 60 min. Another advantage of Fenton reactions is that mineralization is possible in sunlight avoiding the use of UV light. Fenton (Fe²⁺/H₂O₂) and Fenton-like (Fe³⁺/H₂O₂) reactions were compared for both dark and photo-assisted reactions. Penicillin was completely removed after 40 min of advanced oxidation with Fe²⁺/H₂O₂ at pH 3. Higher COD and Total organic carbon (TOC) removals were obtained with dark Fe²⁺/H₂O₂ at pH 3 compared with dark Fenton-like Fe³⁺/H₂O₂. Photo-assisted reactions using UV-C provided only slightly higher removal efficiencies. TOC removal was higher with photo-Fenton reaction and COD removal was slightly higher with photo-Fenton-like reactions. Since Fenton reactions operate at room temperature normal pressure and without the highly complicated
apparatus, there should be a smooth transition from laboratory scale to large scale. On the other hand, the strong dependence on the aqueous solution pH (optimum pH 2-4 for the production of OH\textsuperscript{-} radicals) and on the concentrations of hydrogen peroxide and ferric / ferrous ions and the disposal of the iron sludge are factors which need to be taken into consideration. One possibility is the partial use of Fenton reactions to produce a non-toxic and biodegradable intermediate which could then be treated in an inexpensive biological step to achieve complete mineralisation. [ A. M. Deegan; B. Shaik; K. Nolan; K. Urell; M. Oelgemöller; J. Tobin; A. Morrissey, 2001]

CONCLUSIONS

Various treatment methods for wastewater found in the literature have contributed greatly to our knowledge regarding the fate of these compounds in different treatment systems. Generalizing compound behavior in these systems would allow further characterization of the fate and risk associated with water in the environment, yet this description of trends is hindered by the wide variation in removal efficiencies across therapeutic classes, treatment processes, and even among separate studies for the same individual compounds. The majority of studies summarized used “removal” to describe the elimination of parent pharmaceuticals. The mere disappearance of the parent compound cannot be considered synonymous with complete removal. If adequate controls for physical and chemical removal mechanisms are in place, the loss of the parent compound indicates biotransformation of an unknown degree and not necessarily mineralization. Only monitoring for metabolites or end products of mineralization can provide information about the degree of biotransformation.

The wastewater from pharmaceutical production facilities and municipal wastewater treatment plant are the primary source of API’s in the environment. A significant amount of research in the area has focused on municipal wastewater, as data from municipal wastewater plants are relatively accessible. However, research into wastewaters from pharmaceutical manufacturing plants is more problematic due to difficulties in accessing information. Nevertheless, treatment technologies that work for municipal wastewaters should also be suitable with modification for industrial wastewaters. There are a number of promising new treatments including AOP’s such as oxidation, ozonation, perozonation, direct photolysis, TiO\textsubscript{2} photocatalysis, solar photocatalysis, Fenton reactions and ultrasonic irradiation. These significantly enhance the removal rate of micropollutant from wastewaters. Comparisons among these technologies are problematic since most researchers used synthetic water rather than actual wastewater samples. Research is required in this area to improve treatment efficiencies, identify degradation compounds and to determine the cost and feasibility of full-scale applications. There is also interest in coupling AOPs with more conventional treatments such as activated carbon. Finally, the problem of micropollutant in wastewaters cannot be solved even if it is considerably alleviated - merely by adopting end-of-

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