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Study on treatment technologies for the Removal of Pharmaceuticals from Wastewater by Activated Carbon

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ABSTRACT

In the present scenario, environmental laws have become stringent towards health, economy and reduction of pollution. The pollution is a result of discharge of various organic and inorganic substances into the environment. The sources of pollution include domestic agricultural and industrial water.

The main objective of this study was to conduct an exhaustive review of the literature on the presence of pharmaceutical-derived compounds in water and on their removal technologies. The most representative pharmaceutical families found in water were described and related water pollution issues were analyzed. The performances of different water treatment systems in the removal of pharmaceuticals were also summarized. The water treatment technologies were those based on conventional systems (chlorine, chlorine dioxide, wastewater treatment plants), adsorption/bio-adsorption on activated carbon (from lotus stalks, olive-waste cake, coal, wood, plastic waste, cork powder waste, peach stones, coconut shell, rice husk), and advanced oxidation processes by means of Ozonation, Activated carbon. The effect of these treatments on pharmaceutical compounds and capacity of the used adsorbent has been discussed.

Conventional techniques such as chemical precipitation, carbon adsorption, ion exchange, evaporations and membrane processes are found to be effective in treatment of waste and sewage water. Recently, biological treatments have gained popularity to remove toxic and other harmful substances. The objective of the paper is to make comprehensive review including the performance of each technique in treatment of pharmaceutical waste water. The research directions are also suggested based on the review.

KEYWORDS – Pharmaceutical derived compounds, Activated carbon, Ozonation, ion exchange.

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INTRODUCTION

Pharmaceutical companies are devoted to discovering and developing new medicines that will enable patients to live longer, healthier and more productive lives. But at the same time, they generate both hazardous and nonhazardous wastes, and the insufficient treatment of these wastes leads to surface and groundwater contamination that poses risks to the health of the aquatic ecosystems and the surrounding environment[1,2]. The pharmaceutical compounds reach the aquatic environment as effluents of the hospital structures, pharmaceutical industries, municipal sewage treatment plants, as well as residues of their use in agriculture and breeding[3]. Several investigations have shown evidence that some substances of pharmaceutical are detectable in the environment with concentration levels up to the μg /L due to incompletely removal during conventional wastewater treatment[4,5]. Presently, the effects of pharmaceutical wastes on aquatic organisms are the apparent major concern, including inhibition of growth, production of stress hormone (abscise acid), feminization and behavioral changes[6]. Furthermore, ibuprofen, fluoxethin and ciprofloxacin have been shown to cause mortality of fish in the μg/L range[7].
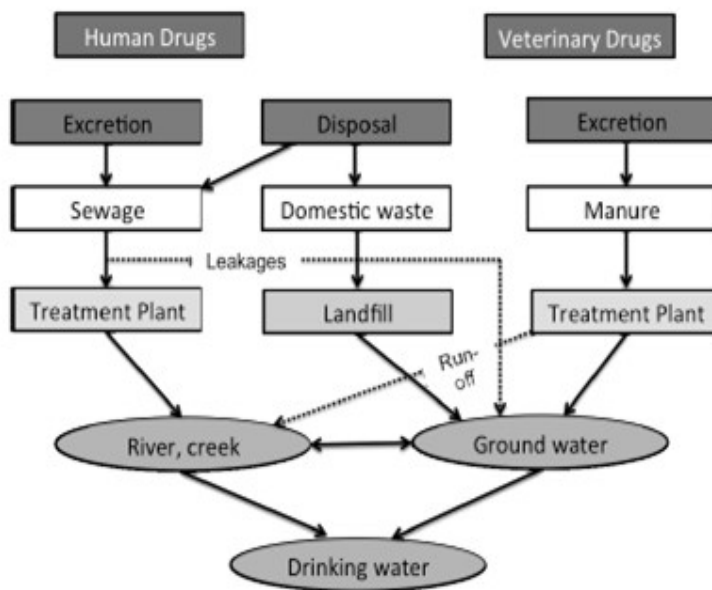

Figure1. The main sources and routes of drugs in the environment

Pharmaceutical drugs are chemicals used for diagnosis, treatment, or prevention of illness of the human body and parts of pharmaceuticals could control symptoms instead of cure conditions. During the most recent decades, tons of pharmacologically active substances were used annually in both human medicine for preventing illness and animal and fish farming as growth promoters or parasiticides[8]. With the addition of new pharmaceuticals to the already large array of chemical

classes, most of these substances are excreted un-metabolized or as active metabolites entering the environment[9]. Indeed, pharmaceutical compounds have been detected in sewage treatment plant effluents, surface and ground water and even in drinking water all over the world[10].

The principal way is through the discharge of raw and treated sewage from residential users or medical facilities. Even though advanced treatment processes are able to achieve higher removal rates, they still do not obtain complete removal of pharmaceuticals[11,12]. After all these various discharge routes and subsequent treatment of wastewater, very low mg/L concentrations of pharmaceuticals have been detected in drinking water supplies[13]. Even through the amount of pharmaceuticals and their bioactive metabolites being disposed or discharged into the environment are probably low, their continual input into the environment may lead to a long-term, unnoticed adverse effect on both aquatic and terrestrial organisms .

Treatment Technologies for Pharmaceutical Removal

The increased awareness regarding adverse effects caused by organic micro pollutants in the aquatic environment, along with approaching legislation, has led to investigations and development of treatment technologies, which could significantly reduce the concentrations of these substances. The two main technologies that are considered, oxidation with ozone and adsorption onto activated carbon, were both commonly used in drinking water treatment however primarily for the purposes of disinfection (Ozonezation) and removal of odor and taste related organics (both)[14,15,16]. In the following sections, these technologies are more thoroughly presented and a few alternatives that have been investigated in the interim are briefly described.

Oxidation with Ozone

Ozone is an unstable gas and must thus be produced immediately before use by e.g. electric discharge of oxygen. Due to the reactive nature of ozone, exposure can pose a significant health risk; chronic exposure to high concentrations can lead to lung damage. In the European Union, the daily exposure limit is set to 120 μg/m3 (~0.05 ppm)[17]. Protective measures to prevent leakage during treatment and sufficient elimination of residual ozone after treatment are therefore required. Ozone has two different mechanisms of action in water matrices; either via direct electrophilic attack by the ozone molecule itself or indirectly by hydroxyl radicals which form during ozone decomposition[18]. Ozone easily targets organic compounds with electron donating groups, such as C=C double bonds, amines or activated aromatic structures, which are found in for example carbamazepine, diclofenac and many antibiotics[19,20,21]. Hydroxyl radicals (·OH) target molecules non-specifically, but only increase the overall reaction rate, not the oxidation capacity at dissolved organic matter (DOM)

levels observed in effluent wastewater[22]. DOM refers to all dissolved organics that are present in a solution, of which pharmaceuticals only contributes a small fraction in wastewater. DOM is quantitatively represented by the concentration of dissolved organic carbon (DOC). The ·OH reaction can be promoted by increasing the ozone dose, raising the pH or by addition of hydrogen peroxide[22]. Furthermore, the oxidation of low to moderately removed substances, which are more dependent on the presence of ·OH, is negatively affected by a relatively high DOC, which scavenge ("neutralize") the radicals. To some extent a high presence of suspended solids could also lead to a reduced performance.

Ozonisation does not lead to complete removal (mineralization) of molecules, but rather degradation into other metabolites. In drinking water treatment, presence of bromide is for example of concern since it is easily oxidized to the carcinogen bromate. Oxidation of pharmaceuticals in wastewater seems to lead to an overall loss of toxicity[23,24], while for some substances an increased toxicity has been observed[25,26]. However, it has been indicated that biologically active sand filters could mitigate this increased toxicity[27].

Adsorption with Activated Carbon

Activated carbon (AC) can be manufactured from a variety of raw materials with high carbon/low ash content, such as coal, lignite or coconut shell. The production process is rather energy consuming and is commonly performed as follows: a slow increase of the temperature to 500°C oxidizes and removes volatile impurities. Further increase of the temperature to 1000°C generates steam, which expands the porous structure of the material. During the activation process a distribution of pores with different size are created which extends from the carbon surface into the particles. Pore sizes are categorized into three categories according to the diameter of the pore opening; micropores are <2 nm, mesopores are 2- 50 nm and macropores are >50 nm. AC is commercially available in either granular or powdered form, defined accordingly: Granular activated carbon (GAC) has a predominantly larger particle diameter than 0.2 mm, while powdered activated carbon (PAC) has particle diameters smaller than 0.2 mm, although typically in the range of 5-50 μm[28,29].

Many different factors related to the adsorbent (the AC), the adsorbate (the adsorbed substance) and the water matrix have been shown to influence adsorption. In the latter, i.e. the wastewater, DOM can have a two-fold negative impact; either pore blocking or direct competition for adsorption sites. The first is attributed to large sized DOM which can block the access to micropores and smaller mesopores, suitable for adsorption of organic micro pollutants. Pore blocking was shown to be mitigated by ACs that had a wide distribution of pores in the size between 30 and

100 nm[30]. Smaller sized DOM directly competes with organic micro pollutants for adsorption sites and can thus increase the AC consumption. For example, it was shown during application of PAC that the DOC-normalized dose (mg PAC/mg DOC) was better correlated to the removal efficiency than the volumetric dose (mg PAC/L)[31]. The use of DOC-normalized doses has also been reported in Ozoneation studies[32].

DOC is reduced in the wastewater treatment stages, primarily by biodegradation as previously described and it was also shown that dosing PAC to effluent from primary sedimentation led to very inefficient adsorption, attributed to very high DOC[33]. Related to the distribution of pore sizes, a large surface area, which is achieved by a high distribution of micropores and small mesopores, was shown to correlate well with the average removal of organic micro pollutants[34]. As during sorption to sludge a higher hydrophobicity (log D), was well correlated with better adsorption to AC, which has a predominantly hydrophobic surface[35]. In the same study, presence of hydrogen donor/acceptor groups and aromatic rings in the molecular structure of the adsorbate was shown to be beneficial for the adsorption, as compared to the absence. Furthermore, inevitable adsorption of DOM tends to give the carbon surface a negative charge at normal effluent pH (3-4), which promotes electrostatic interactions. Thus positively charged substances generally show better adsorption in such conditions than those with negative charge[36,37].

Granular Activated Carbon

Treatment with GAC is normally performed as filtration through one or several fixed bed columns. An important concept for GAC filtration is the mass transfer zone (MTZ), which is where adsorption occurs in the filter bed. The MTZ moves down (or up) the filter bed as the GAC becomes saturated by the adsorbate. If the MTZ extends beyond the filter bed, by applying a high flow or by almost complete saturation, the adsorbate will pass through the filter. Breakthrough occurs at the point when an undesired ratio of effluent to influent concentration (C/C0) is exceeded. The filter bed has then reached its bed life and is replaced. The accumulative volume that has passed through the filter bed, the throughput, is commonly given in bed volumes (BV) of water that has been treated. Bed lives are typically in the range of several thousand BV. The HRT in a GAC filter bed is often given as the empty bed contact time (EBCT), i.e. with the imaginary assumption that the GAC is completely porous. Some parameters, which were shown to reduce the bed life, are (high) presence of DOM, shorter EBCT i.e. higher flow, and temporarily or consistently high pollutant concentrations. The opposite could be achieved with strategic operation such as parallel operation of several filter columns or so-called lead lag operation of filters in series[38]. GAC has the advantage over PAC that it can be regenerated for later reuse. This is done in a process very similar to the

activation process, i.e. thermal regeneration, during which adsorbate are volatilized and degraded. Thus, the adsorption capacity is completely restored, however, at the cost of a ~10% mass loss[39].

Powdered Activated Carbon

Treatment with PAC is normally performed in a system composed of one or several contact tanks where the adsorption primarily occurs; they should therefore be properly mixed. Following the contact tank(s) there is a need for a particulate retention step to prevent AC particles from passing through to the effluent. This may be composed of sedimentation and/or physical filtration. Sedimentation may be aided by application of coagulants and/or flocculants. The main operational parameters of PAC treatment are the carbon dose and the HRT of the water in the contact tanks, i.e. the contact time. An increased dose will naturally increase the adsorption capacity and an increased contact time will allow the adsorption to approach equilibrium. It has been shown that adsorption equilibrium is reached after 20-48 hours[40,41]. As this exceeds even the HRT of many WWTPs, efficient use of the adsorption capacity is not feasible if the retention time of the water and the AC is equal. In GAC filtration, equilibrium is naturally reached as long as there exist an MTZ, since the "carbon dose" is preloaded. To mimic this during PAC treatment the carbon retention time needs to be extended. Nicolet and Rott proposed recirculation of PAC as a solution to this problem nearly two decades ago, when they tried to achieve cost-efficient color removal in wastewater, in a separate pilot system[42]. When the removal of organic micro pollutants during recent years became an emergent topic, this process modification was adapted seemingly by default to achieve an acceptable removal[43].The implication of recirculation in a separate treatment stage (internal recirculation) and the benefit it gives is thus still quite understudied in the large scale[44,45]. An alternative to internal recirculation has however been more explored, involving recirculation to the biological treatment stage[46,47]. If added slightly after the influent to the biological treatment stage, where DOC is already heavily reduced, it was shown that the superior contact time over a separate treatment led to comparable removal, despite an overall higher DOC[38]. This research has solely been conducted in Germany and Switzerland where the digested sludge primarily is incinerated, in contrast to countries like Sweden where the preferred handling of this waste is in conflict with this development. In a full-scale application with a separate treatment stage, spent PAC would continuously be removed from the system, then be dewatered, dried and finally incinerated to limit transfer of the pollutants into another biome.

Table.1 Literature review

Author	Adsorbent	Pharmaceutical	observation	Removaladsorbent or capacity
Liu[48]	GAC LS (from lotus stalks)	Trimethoprim, bacteriostatic antibiotic	Four kinds of phosphorus oxyacids (HxPyOz), i.e. H3PO4, H4P2O7, HPO3 and H3PO3, were used to activate LS	228mg/g
Baccar[49]	GAC (from exhausted olive-waste cake)	Ibuprofen, analgesic Ketoprofen, antiinflammatory Naproxen, antiinflammatory Diclofenac, antiinflammatory	Activated carbon was produced via chemical activation using Phosphoric acid. Increasing pH gradually reduced the uptake of the four drugs. The increase of temperature in the range 4–40 _C does not have a perceptible effect on the adsorption processes	33.25mg/g
Cabrita[50]	GAC B (from coal) NS (from wood) PP (from plastic waste) CC (cork powder waste) CP (from peach stones)	Paracetamol	Samples prepared by chemical activation of biomass residues showed reasonably high removal efficiencies and fast rate of adsorption.	212mg/g
P. Liu, W.J. Liu[51]	Lotus Stalk derivatives	Trimethoprim	Activated with phosphorus oxyacids	79percent
H.R. Pouretedal[52]	Vine woods	Amoxicillin Cephalexin Penicillin G Tetracycline	T = 45 C, pH = 2, 0.4 gL1 AC	88percent
I.Cabrita, B. Ruiz[53]	Coal Wood Plastic waste Powder waste Peach stones	Paracetamol	T = 30 C	74percent 97 percent 60percent 87percent 82percent
Rosal[54]		Ciprofloxacin		98percent

Activated Carbon Variants

A few studies have recently investigated the performance of applications using variants of the conventional activated carbon types which were smaller than the defined particle sizes[55,56]. These modified ACs gave the benefit of faster adsorption kinetics, thus contact times could be shortened while achieving a comparable removal. The adsorption capacity was however generally not affected since the AC particles maintained their original pore size distributions. It remains to be seen whether this is viable alternative in full-scale applications since the suggested particle sizes currently only can be attained by thorough grinding of commercially available products.

Activated Carbon vs. Ozoneation

A few studies have compared the removal of organic micro pollutants with Ozoneation and PAC in bench and pilot-scale[31,32]. Altmann considered both treatments to be well suited for the intended purpose and showed good removal of the critical substances carbamazepine and diclofenac, while Ozoneation was more suited for the removal of sulfamethoxazole and PAC could remove a few substances including benzotriazole better. Margot favored PAC with the extension of ultra filtration (PAC-UF) for particle retention, despite a higher operation cost than Ozoneation, since PAC-UF led to a higher reduction of toxicity in the effluent. Mousel compared the energy demand for application of Ozoneation, GAC and PAC and when combining both energy demands at the WWTPs and the energy demands for production and transportation of raw materials, Ozoneation was the clear winner followed by PAC. For the activated carbon methods it was noted that the energy demand for production and transportation were dominant and that the latter could easily improve in the future if these treatment methods become ubiquitously implemented in wastewater treatment. Implementation of either Ozoneation or PAC was estimated to raise the nation-wide cost for wastewater treatment in Switzerland by 10-15%[57].

ALTERNATIVE TREATMENT TECHNOLOGIES
Oxidation with Chlorine Dioxide

Oxidation with chlorine dioxide (ClO2) for removal of pharmaceuticals was suggested as an alternative to Ozoneation and removal efficiencies was compared between the methods in a few studies[58,59,60]. For most of the evaluated pharmaceuticals ClO2 had lower oxidation rate, which is to be expected since it is a weaker oxidant and does not generate ·OH. However, the capacity to remove substances such as diclofenac, ethinylestradiol, sulfamethoxazole and some other antibiotics were similar to that of ozone, while practically no oxidation occurred of carbamazepine and ibuprofen. Overall, oxidation with ClO2 show few advantages over Ozoneation, however, Hey suggested it could be an alternative to Ozoneation for smaller WWTPs (<2000 person equivalents) depending on future effluent criteria, due to simpler operation and lower estimated operation cost in such a setting.

Nano Filtration/Reverse Osmosis

Filtration with high-pressure membranes, i.e. by nano filtration and reverse osmosis (NF/RO), has been investigated for the removal of pharmaceuticals in wastewater to some extent. These membranes have pores or cavities that allow the permeation of water, but can retain or reject substances based on a combination of size exclusion, adsorption via hydrophobic interaction and via electrostatic interactions[61]. The molecular weight cut-off for the pores is normally in the range of

200-300 g/mol, which theoretically would lead to rejection of many pharmaceutical substances. Electrostatic interactions can occur due to the predominantly negative charge of the NF/RO membrane surface when submerged in a water matrix, such as wastewater. It was shown that this could lead to a better rejection of negatively charged than positively charged molecules, due to diffusion through the membrane of the latter[62]. Overall, a high removal of pharmaceuticals, comparable to that of AC adsorption (and thus Ozoneation) is achievable[63]. However, the energy demand was estimated to be at least 40% higher than that of these technologies and additional treatment of the rejected wastewater fraction (20-25% of the total flow) is needed to ultimately prohibit any discharge, and would further increase the cost of this technology[64]. Thus, substantial optimizations would be required to make NF/RO filtration a competitive alternative to the two main technologies.

Adsorption with Zeolites

Zeolites are porous minerals, which like activated carbon, can act as an adsorbent for organic compounds. Unlike AC however, zeolites have more or less uniform pore sizes, which can be selected in the range of the desired molecular diameters. Thus, zeolites can absorb molecules of a certain size very well. This was shown by de Ridder who in addition could show that organic matter in surface water did not interfere with adsorption by pore blocking, which can be attributed to a more homogenous surface are than that of AC[65]. In conclusion, it was recommended that adsorption with zeolites should only be applied as a complement to e.g. AC adsorption due to the very limited affinity range.

CONCLUSION

An overview of the technologies described in this paper is compiled to allow for a rough comparison. An easy conclusion that also has been drawn is that Ozoneation and activated carbon adsorption are the most suitable options for stand-alone operation. Both technologies have the potential for a high and, perhaps more importantly, broad removal of pharmaceuticals at a relatively low cost. Some of the other technologies, i.e. NF/RO filtration and zeolites adsorption could potentially be considered for combinatorial treatment with the two main alternatives to compliment their shortcomings. In pharmaceutical wastewater treatment "affordable" and "simple" are however key attributes when it comes to extension or optimization of the treatment processes, thus this would probably only be applicable in obscure cases.

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