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EMERGING CONTAMINANTS IN WASTEWATER

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Abstract: Emerging contaminants are micropollutants found in wastewater, such as antibiotics widely applied to prevent or treat human and animal diseases, and steroid hormones used for animal fattening. Anaerobic processes are widely applied in the treatment of swine, cattle and poultry wastewater, but their performance can be diminished by the inhibition effect of antibiotics. Emerging contaminants cannot be entirely removed by conventional wastewater treatment. They accumulate in sludge and manure applied as fertilizers on the agricultural soil, resulting in localized contamination of surface and ground waters. Released in the environment, the emerging contaminants have eco-toxicological effects in aquatic and terrestrial organisms and human health: feminization of aquatic organisms, bacterial resistance, endocrine disruption, neurotoxicity and cancer. Emerging contaminants endanger the reuse of treated wastewater for irrigation of vegetable and energy crops, a regular practice among farmers trying to overcome water scarcity in arid and semiarid areas. The uptake and bioaccumulation of emerging contaminants in plants and fodders and their subsequent entry in the human food chain have been gaining attention over the last decade. This paper provides a review on the existence and the removal of antibiotics and steroid hormones in wastewater via different treatment technologies.
Keywords: emerging contaminants, antibiotics, steroid hormones, wastewater treatment

INTRODUCTION

In arid and semiarid areas, the reuse of wastewater for irrigation is regularly applied by farmers. Micropollutants in municipal wastewater, such as pharmaceutics, personal care products, pesticides, insecticides, surfactants, detergents, dyes, polymers, plastics, phthalates, flame retardants, industrial additives, and the micropollutants in livestock wastewater, such as antibiotics applied to prevent or treat animal diseases and steroid hormones used for farmed animal fattening, are known as emerging contaminants (ECs). Since they cannot be entirely removed by conventional wastewater treatment, the ECs are released into the receiving environments including rivers, fishponds, and crop fields.

Most commonly found molecules of human drugs in treated effluents and the environment include antibiotics, analgesics, contraceptives, anti-cancer agents, beta-blockers, lipid regulator agents, anti-inflammatory drugs, anticonvulsants, contrast agents, hormones and even disinfectants (Deblonde et al., 2011). Chemical, natural, or synthetic antibiotics are widely administered drugs in human and veterinary medicine and in aquaculture to block the multiplication of pathogenic microorganisms or to treat diseases caused by bacteria (Marcelino et al., 2017). More than 150 antibiotics are currently in use, of which over 90% are natural products of bacteria, fungi and semisynthetic modifications of natural compounds, and only a few are entirely synthetic (von Nussbaum et al., 2006). The increasing use of antibiotics and the subsequent development of multi-resistant bacteria pose severe risks to human and animal health (Grenni et al., 2018) and the environment (Pan and Chu, 2017).

The problem of ECs is the lack of knowledge of their impact in the long-term effect on human health and the environment. Antibiotic residues have been frequently identified in rivers, sediments and soils (Michael et al., 2013). Often, antibiotics manufacturers discharge illegally the wastewater in their neighboring environment, causing further contamination to groundwater, waterways, soil and local communities (Pan and Chu, 2017). A preliminary risk assessment database for common pharmaceuticals and their risk to the environment has been developed (Cooper et al., 2008). When these undesirable compounds end up in the environment, they pose risks to all living organisms: antibiotic-resistant bacteria, antibiotic-resistant genes, neurotoxicity, endocrine disruption, cancer, allergic reactions (Martinez et al., 2014) and feminization of aquatic organisms such as fish, alligators and frogs (Orlando and Ellestad, 2014). Endocrine-disrupting products (steroid hormones, antibiotics and other pharmaceuticals) interfere with normal functioning of hormone systems in wildlife and influence plant development (Habteselassie et al., 2013).

Antibiotics cannot be fully metabolized by humans and animals. During their transfer from ingestion by the animal to the environment and then in wastewater treatment processes, antibiotic molecules could undergo transition and degradation. Thus, various unknown metabolites could be produced through different physicochemical processes, i.e. oxidation, hydrolysis, photodegradation and reduction reactions, which might produce compounds with higher toxicity than those of the antibiotics (Cheng et al., 2018). Eighteen antibiotics have been detected in soil, and seventeen in animal manure and biosolids, the most abundant of which was tetracyclines, with 2.68 μg/g in soil and 184 μg/g in manure, as well as ciprofloxacin with 3.26 μg/g in biosolids (Pan and Chu, 2017). Sabourin et al. (2012) have studied the uptake of antibiotics by different crops (potato, carrot, tomato and sweet corn) from field soils previously treated with municipal biosolids and reported sulfonamides, trimethoprim and quinolones with concentrations ranging from 0.02 to 14 ng/g (dw) in the edible parts of the crops. The residual antibiotics may be taken up by crops which can be used for animal or human consumption (Dolliver et al., 2007). Once transmitted in the water environment, the residual antibiotics are toxic to algal and cyanobacterial populations that have crucial roles in the health of aquatic ecosystems (Gonzalez-Pleiter et al., 2013). Long-term exposure to residual antibiotics generates antibiotic resistant bacteria and antibiotic resistant genes, and this is recognized as one of the most serious overall public health issues (Davies and Davies, 2010). The prevalence of resistance to old antibiotics (aminopenicillins, tetracyclines, sulfonamides, or erythromycin) can reach more that 50% of some bacterial populations discharged in the final effluents of WWTPs with conventional treatment (Rizzo et al., 2013). Antibiotics and antibiotic resistant genes are emerging environmental contaminants (Pruden et al., 2006) and they have been detected in soils at depth of 20–30 cm (He et. al., 2019) or 40–60 cm (Tang et al., 2015), showing the transfer of antibiotics and migration of resistance determinants to deeper layers of soil by long-term application of animal manure and biosolids. Antibiotic resistance gene levels in the soil increase after irrigation with wastewater (Dungan et al., 2018). Antibiotic resistant bacteria are considered to be ECs (Pruden et. al., 2006) and they can make their way from the farm environment to humans through occupational exposures on farms and at meat processing facilities, as well as by food borne exposures among consumers, use of animal manures as crop fertilizers, and contamination of surface water and groundwater at animal production facilities (Koch et al., 2017).

In recent years, biocides have also been seen as ECs, due to their widespread use in household products. Biocides have adverse effects on aquatic organisms, such as toxicity to algae, weak estrogenic activity, and potential role as endocrine disruptors due to aromatase inhibition (Oliveira et al., 2017). Exposure of aquatic organisms to ECs may cause sexual disruption, such as feminization, intersex, altered oogenesis (Kidd et al., 2007) and could interfere with their growth, aging, survival and reproduction at ng/L levels in aquatic environments (Biswas et al., 2017). Wastewater treatment plants (WWTPs) are the most important source of ECs in the water environment (Sim et al., 2011). Due to their high solubility, low volatility and low degradability, the ECs can survive wastewater treatment processes in WWTPs and be sorbed by biosolids, which are subsequently applied to agricultural lands as fertilizer.

HUMAN ANTIBIOTICS

In developed countries, the annual consumption of pharmaceuticals per capita is of 50–150 g (Zhang et. al., 2008). Human antibiotics are only metabolized partially and after use, their metabolites are excreted into the sewerage network with 30–90% of the parent compounds in feces and urine, and finally end up in the receiving environment (Zhou et al., 2013), not only in wastewater treatment plants (WWTP) but also in surface waters (Hussain et al., 2012), groundwater and soil. In addition, a significant percent is given by expired and unused medicines, inadequately disposed through sinks and drains (Kümmerer, 2009).

Antibiotics reach water and soil (Figure 1) by discharge of municipal sewage, animal husbandry, manufacturing industry, landfill leachates of antibiotic disposal, runoff from agricultural field containing livestock manure, aquaculture ponds (Ben et. al., 2019), hospital and pharmaceutical wastewater (Gadipelly et al., 2014), irrigation with treated wastewater in arid and semi-arid regions, application of biosolids - manure and sludge - to fertilize the soil (Pan and Chu, 2017; Grenni et al., 2018).

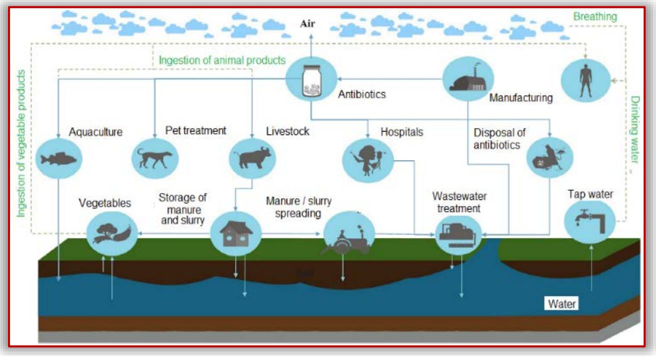

Figure 1 - Human exposure to antibiotic resistance due to antibiotic residues in environment (Ben et al., 2019)

When wastewater, animal manure or biosolids are used in the soil-plant system, the antibiotics might accumulate in irrigated soil, then can be taken up by crops and accumulate in different plant tissues. The uptake and bioaccumulation of pharmaceuticals active compounds in the edible parts of food crops and fodders and their subsequent entry into the human food chain have been gaining prominence over the last decade (Christou et al., 2017).

VETERINARY ANTIBIOTICS

Veterinary antibiotics are extensively used in prevention and treatment of animal diseases, but they are also administered on a large-scale basis, often in feed and water, to enhance productivity, which far outweighs their use as animal therapeutics at present (Gelband et al., 2015). Common antibiotics used as growth promoters in animal breeding are ampicillin, tetracycline, sulfonamide, chlortetracycline and colistin (Tao et al., 2014). Other widely used veterinary antibiotics belong to the following four classes: oxytetracycline (OTC), sul-famethoxazole (SMX), tylosin (TYL), and monensin (MON) (Tasho and Cho, 2016; Pan and Chu, 2017). Globally, the annual usage of antibiotics has been estimated in the range of 100000 and 200000 tons (Kümmerer, 2003). China, the biggest swine (Liu et al., 2012) and poultry (Wei et al., 2011) breeding country in the world, is also the largest producer and consumer of veterinary antibiotics in the world, with annual usage of over 25000 tons in 2007 (Xu et al., 2007) and 84000 tons in 2015 (Zhang et al., 2015). In United States, about 11200 tons of antibiotics are used for non-therapeutic purposes, mostly to promote the growth of poultry, swine and cattle (Kümmerer, 2009). According to the European Center for Disease Prevention and Control (ECDPC), in 2014, the consumption of veterinary antibiotics in Spain, Italy, and Germany was of 2964, 1432, respectively 1306 tons; the lowest consumption and the lowest consumption were recorded in Luxembourg (2.1 tons) and Iceland (0.6 tons) (Pan and Chu, 2017). In 2030, China would still be the largest consumer of antibiotics in food-producing animals, followed by the USA, Brazil, India and Mexico (van Boeckel et al., 2015).

Given their over-dosage and low assimilation, 70–90% of veterinary antibiotics are excreted into the environment with animal wastes (urine and manure) and thus threaten the health of humans and other organisms by inducing the prevalence of antibiotics resistant bacteria and genes (Cheng et al., 2018). It was estimated that the antibiotics residue excreted from a swine was about 18.2 mg/day (Zhou et al., 2013). Moreover, antibiotics do not emerge in swine wastes individually, but with many other types of antibiotics or toxic pollutants, for example with hormones or heavy metals (Zhang et al., 2017).

Due to the effectiveness, broad-spectrum and favorable price, sulfonamides, tetracyclines, fluoroquinolones, macrolides (Chen et al., 2012) and other antibiotics (bacitracin, lincomycin, ormetoprim and trimethoprim) were extensively used in swine industry (Zhang et al., 2015). These antibiotics have different operation modes on microorganisms, such as interfering with the functions of cell membranes, blocking protein synthesis and preventing nucleic acid synthesis (Cheng et al., 2018). The maximum concentrations of sulfonamides, tetracyclines, fluoroquinolones and macrolides have ranged from 23.8 μg/L to 685 μg/L, with some varying from trace amounts to those as high as the ppm levels in manure slurry (Chen et. al., 2012). In liquid swine manure, concentrations of tetracycline from 14 to 41 mg/kg, chlortetracyclinefrom 0.9 to 1.0 mg/kg, and sulfamethazine at 7.2 mg/kg were reported (Hamscher et al., 2005). Tetracyclines from 0.05 to 15.7 μg/g and sulfonamides from 0.015 to 2.1 μg/g were discovered (Jacobsen and Halling-Sorensen, 2006). Oxytetracycline, erythromycin, florfenicol, sarafloxacin, premix, sulphonamides are commonly used antibiotics in aquaculture (Kumar and Pal, 2018).

The possible remanence of veterinary antibiotics in the environment is influenced by animal excreta, soil type, pH, temperature and UV light. Some antibiotics, for example fluoroquinolones and sulphonamides, are very strongly adsorbed by animal faeces and manure, and they remain unaltered even with increased aeration and temperature in the manure, thereby spreading into the environment in their original active form (Tasho and Cho, 2016). To reduce the environmental and health risk of antibiotics, their use as animal growth promoters has been forbidden in the E.U countries (Alban et al., 2008) and in the United States (FDA, 2003). Current legislation at European level does not contain an antibiotic concentration requirement for discharge from WWTPs to receiving water (Carvalho and Santos, 2016). However, the E.U Water Framework Directive 2015/495 requires those responsible for wastewater treatment to monitor the presence of emerging pollutants with the future aim of improving the quality of the effluent released to surface waters (Acheampong et al., 2019).

STEROID HORMONES

Steroid hormones can interfere with the endocrine function in organisms at low concentrations (Wu et al., 2017). Natural steroids are mainly originated from the feces and urine of human, livestock and aquaculture (Liu et al., 2009). Some natural and synthetic steroids have been used in human daily life for contraception and therapy, and in livestock production to prevent and treat diseases, to promote growth and to improve productivity (Liu et. al., 2012) and animal breeding control (Liu et al., 2015). Natural and synthetic steroid hormones, which are proved to induce biological effects on some organisms at part per trillion concentrations (ng/L), are poorly eliminated by conventional wastewater treatment processes (Fatta-Kassinos et al., 2011). Steroids are estrogens, androgens, glucocorticoids and progestagens. Estrogens, a group of endocrine disrupting compounds (Amin et. al., 2018), are natural (estrone, 17β-estradiol and estriol) when are produced in humans and animals, and synthetic (17α-ethynil estradiol) used as birth-control drugs (Zheng et al., 2008). Women daily excrete 10–100 μg of estrogen, and excretion increases up to 30 mg during pregnancy. The average human excretion of estrone and 17b-estradiol was 10.5 μg/day and 6.6 μg/day (Tiwari et al., 2017). In influents, the concentrations of estrone, 17β-estradiol and 17α-ethynil estradiol were measured in ranges from 2.4–116, 4–150 and n.d-14.4 ng/L (Amin et al., 2018). In effluents, the concentrations of estrone, 17β-estradiol and 17α-ethynil estradiol were measured in ranges from n.d-96, n.d-30, and n.d-5 (Combalbert and Hernandez-Raquet, 2010). It was found that 10–100 ng/L concentrations of natural estrogens have an effect on the levels of the estrogenic exposure biomarker, vitellogenin, in fish (Cai et. al., 2013).

Dairy cows are the largest contributor of excreted estrogens in comparison to pig, sheep and chickens (Cai et al., 2013). Sewage and livestock wastewater are major pathways of estrogens in aquatic environment (Zheng et. al., 2008). Progestagens are growth promoters that improve the efficacy of feed conversion in animals through increasing bone density and muscular mass (Yang et al., 2009). The E.U, Netherlands and China have prohibited the administration of steroid hormones for farmed animal fattening due to adverse human health effects of hormone residues in animal meats (Liu et al., 2015).

REMOVAL OF EMERGING CONTAMINANTS FROM THE WASTEWATER

Different types of treatments are currently being tested to effectively remove the ECs from wastewater, with the lowest possible economic cost, before being discharged into the ecosystems. Tertiary treatment technologies (ozonation, chlorination, ultraviolet, membrane technologies, sand filters) are the most promising options for reducing ECs.

The conventional activated sludge (AS) and anaerobic digestion (AD) processes are ineffective for antibiotics and hormones removal, and they can still pose risks to the surrounding environment (Figure 2). Nevertheless, AD systems can degrade the antibiotics in swine wastewater to various degrees, depending on the initial concentrations and classes of antibiotics, type of bioreactor and operating conditions. More attention should be given to the toxic effect of antibiotics on micro-organisms involved in anaerobic processes of wastewater treatment. The presence of antibiotics in anaerobic processes changes the microbial structure by altering microorganisms to less sensitive ones to specific antibiotics or by promoting strains with antibiotic resistant genes (Angenent et al., 2008). In biological treatment, biosorption and biodegradation are two major mechanisms for antibiotics and hormones removal (Cheng et al., 2018). Biosorption and biodegradation followed by the removal of excess sludge can be considered for the removal of the estrogens in WWTPs (Luo et al., 2010), with reported removal rates between 19-98% for estrone, 62-98% for 17β-estradiol and 76-90% for 17α-ethynil estradiol (Mohagheghian et al., 2014).

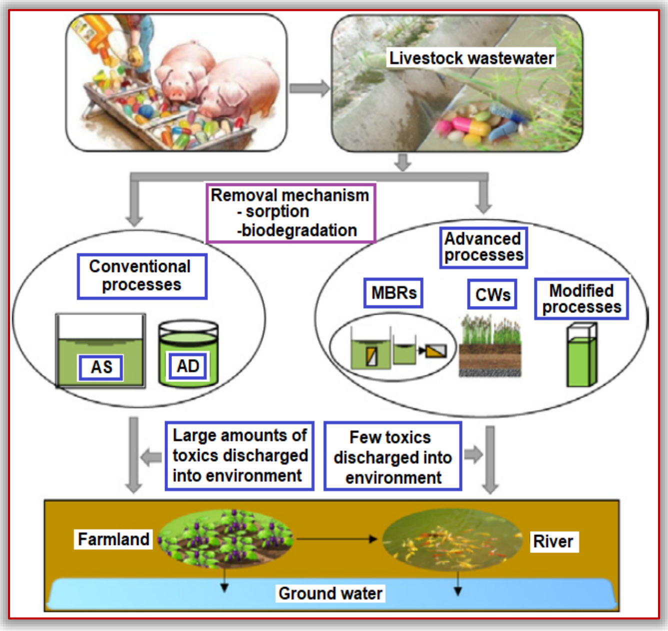

Figure 2 - Removal possibilities of antibiotics and hormones from swine wastewater (Cheng et al., 2018)

Membrane bioreactors (MBRs), constructed wetlands (CWs), stabilization ponds and modified processes perform better due to higher biodegradation of toxicants (Cheng et al., 2018). Microalgal-bacterial processes developed in photobioreactors have recently been recognized as environmentally friendly and cost-effective alternative for ECs removal from wastewater, especially at: high sludge retention time (4–20 days), enhanced penetration of UV light as a result of their high surface area to volume ratios, high daily variations of pH (between 7–11), 2–25 mg O_2/L dissolved oxygen concentration (Norvill et al., 2017). Ibuprofen, naproxen, salicylic acid, triclosan and propylparaben were removed by photodegradation in novel algal-bacterial photobioreactors (Lopez-Serna et al., 2019).

Lagoons as secondary or tertiary treatment have proved to be viable solutions for estrogens removal from livestock wastewater. Large-scale CW systems can effectively remove antibiotics, antibiotic resistant genes, non-steroidal anti-inflammatory drugs, analgesics, stimulants, psychoactive drugs, highly chlorinated compounds (Zhang et al., 2012). The presence of plants in CW improves the removal capacity for pollutants by direct absorption, by providing retention sites and by increasing microbial activities (Carvalho et al., 2014). Vertical subsurface flow CW obtained higher antibiotic removal efficiencies than horizontal subsurface flow and free water surface flow counterparts (Liu et al., 2014).

Antibiotic resistant genes (tetracycline and macrolide-lincosamide-streptogramin B) arising from swine-feeding operations can survive typical animal waste treatment processes, because their levels remained high in swine wastes during composting (Wang et al., 2012), lime stabilization, anaerobic digestion (Tao et al., 2014), constructed wetlands (Liu et al., 2014) and lagoons (Brooks et al., 2014). Membrane processes (reverse osmosis and nanofiltration), have been effective in the removal of different ECs and allow the separation of divalent and monovalent ions from wastewater. In a feasibility study of removing antibiotics (norfloxacin, ofloxacin, roxithromycin and azithromycin) from a WWTP by secondary treatment followed by nanofiltration were obtained up to 98% removal rates (Liu et al., 2014). Photocatalytic oxidation, intermittent sand or coke filters can remove the ECs from wastewater (Egea-Corbacho et al., 2019).

Adsorption on activated carbon, ozone-based advanced oxidation, photooxidation, radiolysis and electrochemical oxidation have been tested at lab and industrial scale to remove the ECs from wastewater, but toxic by-products are formed and these technologies are quite expensive to be widely applied in WWTPs (López-Serna et al., 2019). Adsorption on multi-walled carbon nanotubes was studied to remove 1,8-dichlorooctane, nalidixic acid and 2-(4-methylphenoxy) ethanol (Patino et al., 2015). Indomethacin, diclofenac, betablockers (atenolol, metoprolol and propranolol), which are poorly removed in AS conventional treatment, showed large ozonation rates and were removed from treated wastewater using moderate ozone doses (Rosal et al., 2010). Electrooxidation using boron doped diamond electrodes is a promising technology to reduce Ecs in wastewater sludge (Barrios et. al., 2015). Acetaminophen and sulfonamide were removed from wastewater using spent mushroom compost of Pleurotus eryngii (Chang et al., 2018).

CONCLUSIONS

The presence of emerging contaminants, a category of micropollutants that include any chemical that is not usually monitored in the environment, was observed in treated wastewater effluents, aquatic environments and soil. Even at low concentrations, the emerging contaminants can increase the resistance among microorganisms and can have a significant impact on the aquatic ecosystems and human health. The development of antibiotic resistant bacteria and antibiotic resistant genes also pose an increasing concern. Although intensely studied, there are still knowledge gaps in the ecotoxicological effects of antibiotics and hormone steroids.

Conventional WWTPs, usually based on biological processes, are unable to fully remove the emerging contaminants from wastewater. Tertiary treatment technologies are the most promising options for reducing ECs. Future research must concentrate on developing sustainable and innovative treatment processes to increase the removal efficiency of emerging contaminants in WWTPs.

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