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'LOW CONCENTRATIONS OF HIGH PRIORITY' – PHARMACEUTICAL AND PERSONAL CARE PRODUCTS (PPCPs); OCCURRENCE AND REMOVAL AT WASTEWATER TREATMENT PLANTS

Låga koncentrationer av högprioriterade ämnen – farmaceutiska och personhygieniska produkter; förekomst och eliminering i avloppsreningsverk

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Abstract

Development of advanced analytical tools and analysis of wastewater samples confirmed the presence of residual amount of pharmaceuticals in environment and WWTP effluent in many European countries. Significant amount of compounds (30–90 % of administrated dose of antibiotics) is transported as active substance via urine. Only some part of taken drug dose is metabolized by organisms and the rest is excreted in changed or unchanged form. Many non-target organisms, that could share some receptors with humans, could be exposed on pharmaceutical activity. Another important issue discussed is the combination of additive, synergistic and antagonistic effect that might reveal in the mixture of pharmaceutically active compounds introduced to the environment. The objective of this paper is to give the overview of recent published data concerning PPCPs. In order to find the efficient technology for removal of residual amount of pharmaceuticals the studied methods and solutions are presented. The most interesting removal system is based on membrane technology. Separation of micropollutants onto membrane surface gives satisfactory results in experiments. A polishing step seems to be also a very attractive technology for treatment of biologically active substances that pass all the preceding steps in conventional WWTPs.

Key words – ecotoxicology, membrane technology, pharmaceutical residues, wastewater

Sammanfattning

Analys av vattenprover med hjälp av olika avancerade analysmetoder har påvisat rester av läkemedel i naturen och i utgående renat avloppsvatten i många europeiska länder. Signifikanta mängder av substanserna (30–90 % av tillförd dos av antibiotika) transporteras ut via urinen som aktiv substans. Endast delar av den intagna läkemedelsdosen metabolitseras i kroppen och resten utsöndras i förändrad eller oförändrad form. Många organismer, som kan dela några receptorer med människan, kan på så sätt bli exponerade för farmaceutisk aktivitet. En viktig fråga är kombinationen av additativa, synergistiska och antagonistiska effekter, som kan uppkomma i naturen vid en blandning av farmaceutiskt aktiva substanser. Syftet med artikeln är att ge en översikt av nyare publicerade data om farmaceutiska och personhygieniska produkter (PPCPs). Studerade metoder och lösningar för att ta bort läkemedelsrester presenteras. Membranteknologin är den mest intressanta elimineringsprocessen. Försök visar på tillfredsställande resultat med avskiljning av mikroföroreningar på membranytor. Ett slutligt polersteg vara en tilltalande metod för behandling av aktiva substanser som passerar de föregående stegen i ett konventionellt avloppsreningsverk.

Introduction

Wastewater treatment plant (WWTP) systems nowadays have to overcome not only the problem of high nitrogen and phosphorus concentration but also the presence of micropollutants in the wastewater. An increasing attention has been paid to the quality of wastewater treatment plant effluents, often with surface waters as recipient. Pharmaceutical and personal care products (PPCPs) are widely used in the human health sector, households and in animal husbandry. Nowadays an increasing consumption of drugs, antibiotics, pain-killers, food additives, personal care products and cosmetics could be observed. Their active ingredients include prescription drugs and also diagnostic agents, 'nutraceuticals', fragrances, sun-screen agents and many others. Pharmaceutical compounds and its active metabolites can be introduced to aquatic environment as a mixture of organic compounds with the effluents, treated and untreated sewage. Some of PPCPs can be persistent and present in the environment in small quantities in the range of ng/l – µg/l. Even small quantities of substances could accumulate and be persistent in the water and may cause some damage to the living organisms. The removal efficiency of different substances in conventional wastewater treatment facilities, the biological step and polishing should be investigated to find an efficient removal strategies. The modification and variation of operational parameters and conditions may change the efficiency, e.g. combination of anoxic/aerobic step and solids retention time and introduction of complementary treatment methods.

Characteristics of biologically active compounds

Pharmaceuticals have been divided into different classes depending on chemical structure, biological activity and application: antibiotics, antineoplastic, analgesic anti-inflammatory drugs, blood lipid regulators, beta-blockers, antidepressants, antiepileptics, impotence drugs, diagnostics contrast media and hormone disruptors (EPA, 1997). Antibiotics are widely used medicines for humans, in veterinary, animal husbandry and aquaculture. Accordingly to studies performed by Halling-Sørensen et al. (1998), Hirsch et al. (1999) and Ternes (1998), antibiotics seemed not to be persistent during sewage treatment, although they were found in the WWTP effluents in low concentrations. Analgesic anti-inflammatory drugs are used as 'pain-killers', probably the most widely used medicines (ibuprofen, diclofenac, naproxen, paracetamol). Carbamazepine as the most common antiepileptic drug has been found in sewage treatment effluent and observed to be extremely persistent. Antineoplastic drugs – anti-cancer medicines are used more often in hospitals for chemotherapy than in households. They are designed to kill the cells, and exposed in aquatic environment they could act as mutagens (Daughton and Ternes, 1999). Other drugs used mostly in hospital are defined as diagnostic contrast media. Iodinated aromatics like iopromide, are very stable biochemically and they tend to excrete without being metabolised (Daughton and Ternes, 1999; Directorate-General Environment, 2001).

Personal care products (PCPs) can be defined as marketed chemicals used as active ingredients or additives in cosmetics, toiletries and fragrances. Triclosan as a non-prescription antibacterial agent has been used over 30 years in toothpastes, soaps, deodorants, detergents, body washers, acne creams (Clearasil), lotions and even for footwear. It is used in hospitals, households, livestock breeders and textile companies as well.

Origin and exposure in the environment

Pharmaceuticals, its metabolites, conjugates or unchanged forms are excreted through urine and faeces. Biologically active compounds mainly enter the environment through disposal of wastewater. Sewage sludge, containing some amounts of biologically active compounds, used as fertilizer can be a convenient option as transporting system for drugs to environment. Antibiotics used in fish farms are exposed directly to the receiving water, as well as food additives from poultry farms and spray drift from tree crops. Personal Care Products and detergents are directly released to water bodies via washing, bathing or swimming (EPA, 2001).

Pharmaceutical substances and Personal Care Products, produced in large quantities and widely used, are sometimes overdosed. In many countries data about annual production and consumption of drugs is usually not available. However, only in Germany 100 tones of human drugs were prescribed in 1995 (Ternes, 1998). Between 1988 and 1993 the total usage of antibacterial substances in Sweden amounted to approximately 35 tones annually, coccidiostatics around 10 tones annually and other antiparastatics to 7.7 tones annually (Halling-Sørensen et al., 1998). Annual production of personal care products, which are available without any limitation, only in Germany in 1990 amount to 550 000 tones (Daughton and Ternes, 1999). This amount can dramatically increase due to a possibility of purchasing drugs without a prescription.

Table 1. *Consumption of pharmaceuticals in Defined Daily Dose system (DDD) for 1000 inhabitants in selected countries (n.a.- not available) (OECD Health Data, 2004).*

	Antide-pressants	Drugs used in diabetes	Diuretics	Cholesterol reducres	Cardiac glycosides	Beta-blockers	Anxio-lytics	Antibac-terials	Analgesics
Denmark	46.5	26.0	106.0	29.5	7.0	24.2	22.1	14.7	89.7
Finland	43.7	52.5	61.5	54.1	7.9	63.9	31.5	22.1	29.7
Sweden	59.5	40.9	84.1	55.9	55.9	49.4	16.3	16.9	75.6
Norway	n.a.	32.3	42.6	85.5	85.5	38.1	n.a.	17.1	49.5
Belgium	45.6	35.3	42.0	74.6	6.2	62.3	n.a.	24.5	10.2
Australia	56.2	39.5	46.9	118.3	6.2	23.9	13.9	20.8	26.3

In Table 1 the consumption of different classes of drugs in Nordic countries in comparison to Belgium and Australia is presented. Sweden is a leading country in antidepressants consumption and on the second place concerning drugs used in diabetes, diuretics, cardiac glycosides and pain killers.

Taking into consideration data published by The National Agency for Medicines (Finish Statistics on Medicines, 2004) consumption of for example antidepressants increased from 7 in 1990 to 48 DDD/1000/day in 2004, 4 DDD/1000/day of statins in 1990 has raised to 65 in 2003 (DDD=Defined Daily Dose). Not so rapid raise was observed for antiinflammatory analgesics and amounted from 45 in 1990 to 75 DDD/1000/day in 2004.

Occurrence in water and wastewater

In four European countries (Italy, Greece, France and Sweden) a monitoring campaign of WWTP effluents was carried out. The results have been reported and have shown that more than 20 individual pharmaceutical products from different therapeutic classes have been found in the effluents (Andreozzi et al., 2003). The majority of β-blockers and antibiotics, gemfibrozil, ibuprofen, naproxen, carbamazepine have been determined in all samples. Furthermore, the occurrence of 32 drug residues belonging to different medicinal classes has been found in German WWTP discharges, rivers and streams (Ternes, 1998). This is only 1% of the pharmaceutical compounds that are approved (approximately 2900 drugs) for the use in human medicine sector.

Hormones such as: 17α-ethylestradiol, 17β-estradiol and estrone were detected in wastewater treatment plants, surface water and rivers (Boyd et al., 2003; Carballa et al., 2004; Ternes, 1998; Ternes et al., 1999a). A first signal about the endocrine disrupting character effect of hormones was noticed in UK rivers, when deformities in fishes were observed (Gomes et al., 2003). These observations support the conclusion that hormones and other disrupting compounds are persistent in the surface waters.

Investigations conducted in a cooperation of the three largest WWTPs in Sweden has shown presence of pharmaceuticals and other organic pollutants in the sewage (Paxéus, 1996). The author presented a list of 137 identified compounds with a spectrum of non-regulated organic pollutants. The list included aromatic hydrocarbons, food and household related compounds, solvents, plasticisers, flame retardants, preservatives, antioxidants and washing and cleaning related compounds (within the range of 0.5–50μg/l). Table 2 presents an overview of analyzed different water samples and determination of pharmaceutically active compounds in the environment.

Ecotoxicological assessment and toxic effects

It should be pointed out that information about behavior of particular compounds in the environment and ecotoxicilogical characteristics is usually not available or need to be investigated.

Synthetic hormones mainly used in contraceptives pills and estrogens-replacement therapy, are described mainly as endocrine disruptor compounds (EDCs) (EDSTAC, 1998). Those compounds are designed to bind to the specific receptor and regulate the metabolic activities. Hazardous effects could be observed on non-target aquatic organisms. Long lasting exposure of estrogens compounds might induce feminization in males, hermaphrodite characteristics (Directorate-General Environment, 2001).

There is a strong evidence that for some fish population the human hormones (17β-estradiol and estrone) which pass through WWTP may be causative agents in eliciting endocrine-mediated effects (Juberg, 1999). In the paper presented by Alcock et al. (1998) it is clearly

Table 2. *Biologically active compounds detected in WWTP effluents (* median value).*

Type	Compound	Concentration [µg/l] in WWTP effluent	References
antibiotics	sulfamethoxazole	2.5 *	2
	eritromycin – H_2O	0.40 *; 0.90; 0.62±0.04	2, 3, 6
	trimethophrim	0.32–0.66; 0.34±0.04	2, 6
antiepileptic drug	carbamazepine	2.1 * ; 1.63 (Berlin), 1.13 (max 1.67)(Austria); 0.54–0.2 (France); 0.18–1.03 (Greece); 0.1–0.34 (Italy); 0.94 (Denmark); 0.15–1.5 (Sweden)	4, 3, 8, 12, 12, 12, 12, 12
anxiolytic drug	diazepam	0–0.04 * ; <1	4, 1
anti-inflammatory drugs	diclofenac	1.3±0.1*; 2.51; 1.84 (max 3.0) (Austria); 0.14–0.89 (Greece); 0.47–1.48 (Italy); 0.16–0.19 (Sweden)	6, 3, 8, 12, 12, 12
	ibuprofen	0.37*; 0.1 (Berlin); 0.13±0.03; 0.012 (max 0.035) (Austria); 0.02–1.96 (France); 0.05–0.1 (Greece); 0.15–0.49 (Sweden); 0.02–0.18 (Italy)	4, 3, 6, 10, 12, 12, 12, 12
	naproxen	0.30*; 0.08 (Berlin); 0.08–0.11 (Louisiana); 0.1±0.01; 0.25–0.88 (Sweden); 0.51–0.92 (France); 0.29–1.51 (Italy)	4, 3, 9, 6, 12, 12, 12
β-blockers	metoprolol	0.73*; 1.7±0.04 (Germany); 0.01–0.08 (France); 0.19–0.39 (Sweden)	4, 7, 12, 12
	propanolol	0.17 *; 0.38–0.47 (Greece)	4, 12
	atenolol	0.1–0.73 (Italy)	12
lipid regulators	bezafibrate	2.2*; 0.05 (max 0.13)(Austria)	4, 7
	gemfibrozil	0.40 *; 0.07 (Berlin); 0.06–0.73 (France); 0.51–0.84 (Italy); 0.18–0.60 (Sweden); 0.23–0.71 (Greece)	4, 3, 12, 12, 12, 12
metabolite of lipid regulators	Clofibric acid	0.36 * (WWTP effluent), 0.48 (Berlin); 0.12 ± 0.02	4, 3, 6
polycyclic musks	tonalide	0.14 (max 0.19) (Austria)	8
	galaxolide	6 (Sweden); max 0.53 (Austria)	11, 8
antibacterial agent	triclosan	0.5; 0.01–0.02 (Louisiana); 0.17–0.43 (France); 0.13–0.16 (Sweden); 0.37–0.70 (Italy)	4, 9, 10, 12, 12
psychomotor stimulants	caffeine	33 (Sweden); ~1; 16–292; 0.18 (Berlin)	11, 1, 1, 3
hormones	estrone	0.009*(max 0.07) (Germany); max 0.048 (Canada);	5
	17α-estradiol	max0.03* (Germany); 0.006 * (max 0.064) (Canada)	5
	17-α ethinylestradiol	0.001* (max 0.015) (Germany); 0.009 * (max 0.015) (Canada)	5
X-ray contrast media	iopromide	0.036 (max 0.18) (Austria)	8

References: 1 Halling-Sørensen et al. (1997); 2 Hirsch et al. (1999); 3 Heberer (2002); 4 Ternes (1998);5 Ternes et al. (1999a); 6 Ternes et al. (2003); 7 Ternes et al. (2004); 8 Kreuzinger et al. (2004); 9 Boyd et al. (2003); 10 Boyd et al. (2004); 11 Paxéus (1995); 12 Paxéus (2004).

stated that male fish exposed on the domestic sewage effluent with 17β-estradiol, estrone, ethinyloestradiol developed hermaphrodite characteristics.

Except for endocrine disrupting compounds that are presumed to be harmful for living organisms like fish and invertebrates, antibiotics is a group of drugs that in aquatic environment may develop multi-resistant strains of bacteria due to genetic changes and drug-resistivity. Bacterial resistance to the antibiotics in the sediments is often found near fish farms, where feed additives for fish are widely used (Halling-Sørensen et al., 1998).

There is a wide range of therapeutic pharmaceuticals that could be available without prescription all over the world. Viagra is a drug for treating impotence by indirectly relaxing the muscles and increasing the flow of blood. The effect on non-target organisms is still unknown and disruption effect of this phosphodiesterase should be concerned regarding the availability over the Internet and the high potential for environmental exposure (Daughton and Ternes, 1999).

Ferrari et al. (2003) suggested that for pharmaceuticals, which are found in active forms, chronic effect studies based on specific endpoints are more adequate. Especially for those compounds that are introduced to aquatic environment in very low concentrations, test like biomarkers, long-term exposure and multigeneration test should be taken into consideration. Furthermore, concerning the persistence of personal care products and its bioaccumulation character, monitoring campaign and environmental risk assessment should be applied (Daughton and Ternes, 1999).

Studies performed by Sanderson et al. (2003) indicated that more than 50 % tested pharmaceuticals were intrinsically toxic and EU labeling is highly required. Ecotoxicological (Quantitative) Structure Activity Relationship ((Q)SAR) screening (ECOSAR) of all pharmaceutical compounds reported in aquatic environment could be a suitable tool for risk assessment and management of pharmaceuticals (Länge and Dietrich, 2002; Sanderson et al., 2003).

The classification of drugs on biodegradation, bioaccumulation and ecotoxity is introduced also by Stockholm County Council, Sweden. The purpose is to increase the awareness of patients, doctors and pharmaceutical companies that pharmaceuticals may pose the risk for non-target organisms (Wennmalm and Gunnarsson, 2005).

Behavior during treatment processes

A large variety of pharmaceutical and personal care products has been determined in WWTP effluent in concentration of several µg/l (Hirsch et al., 1999; Table 2). Due to various chemical and physical properties of compounds, they may evaporate into the atmosphere (ethers), adsorb onto primary and secondary sludge, and spread on land and in small quantities pass through the treatment facilities and be persistent in surface water. It has to be mentioned that biologically active compounds used to be very changeable during their way into water collectors. Furthermore, as it was investigated by Alcock (1999), pharmaceutical compounds have a wide variety of activities, structures, biodegradation paths and they can act synergistically.

Pharmaceutical compounds and medical substances show by lipophilicity, persistence and bioacculumation its physio-chemical behavior in the aquatic environment. Fate of compounds depends on particle-contaminant interactions. Trace pollutants are preferable found associated with dissolved colloids and readily adsorbed and settle with the natural sediments (clay, sediments, microorganisms) and added to the medium (activated sludge, activated carbon). Therefore, the transportation of compounds to wastewater solid phase and its partitioning lead to the increase of removal efficiency. As Jacobsen and Schäfer (2002) noted, most of the compounds are removed due to adsorption to the activated sludge and less than 10 % is removed due to biodegradation.

Many authors suggested that the most important removal mechanism of active compounds is biotransformation (Sedlak et al. 2001; Graaf, 2001; Ternes, 1999b; Schäfer et al., 2002). Because of their chemical properties and different biodegradability mechanisms and potential there is a need to investigate and determine their removal in particular treatment facilities. In Table 3 a summary of pharmaceuticals with removal rates during different treatment systems in shown. As it was reported by Ternes (1998) elimination of PPCPs in municipal WWTPs is sometimes incomplete, e.g. removal efficiency of polar compounds ranging between 60 % and 90 %. The main factor that differs the removal efficiency is ability to adsorbtion and interaction with solid particles or added medium, such as activated carbon. Compounds with very week adsorption coefficients pass the treatment facilities.

Another sampling and analyzing campaign in South of Sweden was performed to evaluate the removal rates of pharmaceutically active compounds in Källby wastewater treatment plant (Bendz et al., 2005). Metoprolol, propanolol and carbamazepine although theirs low excretion rates showed an extremely high persistence in aquatic environment.

It was also observed that synthetic hormones were transformed into biologically active form at the effluent and not degraded during treatment process. The concentration of natural and synthetic hormones is rather

Table 3. *Removal efficiency of biologically active compounds during wastewater treatment with different types of removal processes (B-biodegradation, A-adsorption).*

Compound	Stage	Removal efficiency	References
triclosan	activated sludge (B)	63–88 %	1
	rotating biological contractors (B)	25–30 %	1
	sorption to primary sludge (A)	39–46 %	1
ibuprofen	biological step (B)	60–70 %	2
	trickling filter (B)	22 %	3
	activated sludge	75 %	3
	sewage treatment (B)	inherently degradable	
naproxen	biological step (B)	40–55 %	2
	biological filter (trickling filter) (B)	15 %	3
	activated sludge (B)	75 %	3
	sewage treatment (B)	non-biodegradable	4
paracetamol	sewage treatment (B)	readily degradable	4
estrogen	persistent in sewage and lake water	–	4
17β-estradiol	biological step	~47 %	2
	aerator tank (Brazil)	99.9 %	5
	treatment plant (Germany)	64 %	5
17α-ethinylestradiol	biological filter (Brazil)	64 %	5
	treatment plant (Germany)	passing	5
diclofenac	biological filter (trickling filter) (B)	~9 %	3
	activated sludge (B)	75 %	3
	treatment process	17 %	3
	aeration tank (B)	99 %	6
clofibric acid	biological filter (trickling filter)	15 %	3
	activated sludge	34 %	3
	treatment process	–	6
clofibrate	sewage treatment (B)	non-degradable	4
bezafibrate	biological filter (trickling filter)	27 %	3
	activated sludge	50 %	
tonalide, galaxolide	activated sludge (A, high adsorption coefficient)	80 %	7
caffeine	treatment process (B)	99.9 %	6
	sewage treatment	readily degradable	4
sulfamethoxazole	sewage treatment (B)	non-degradable	4
tetracycline	sewage treatment	non-degradable	4
aspirin	sewage treatment (B)	inherently degradable	4

References: 1 Thompson et al. (2005); 2 Carballa et al. (2004); 3 Stumpf et al. (1999); 4 Halling-Sørensen et al., (1998); 5 Ternes et al. (1999a); 6 Heberer (2002); 7 Kreuzinger et al. (2004).

Table 4. *Advanced processes for treatment of WWTP effluent* (modified after Graaf, 2001; Guo et al., 2004).

Type of process	Principle	Removal	Application	Status	Cost
activated carbon	adsorption	soluble compounds, micropollutants	removal of micropollutants	available	high
chlorination	chemical oxidation	organic substances, micro-org.	disinfection	available	low
deep bed filtration	filtration, biol. oxidation	SS (90–95 %) ammonia	polishing	available, optimization	low
primary membrane filtration	ultrafiltration microfiltration	SS (100 %) bacteria (100 %) viruses (100 %)	qualified purpose	development	high
advanced membrane filtration	reverse osmosis, ultrafiltration	soluble compounds (100 %)	high purity water	development	high
microsieves	sieving bed filtration	SS (60–70 %)	reduction of SS	available	low
reed bed filters	biological filtration	broad spectrum	polishing	available	high
ozonation	chemical oxidation	organic subst., micro-org.	disinfection	available	high
UV	radiation	micro-org.	disinfection	available	medium
polishing ponds	biological sedimentation	broad spectrum	polishing	available	high

low, ranging around few a ng/l, but still they are widely used and extremely persistent in aquatic environment (Alcock et al., 1998).

Advanced treatment techniques for PPCP's and EDC's removal

There is a broad number of methods for PPCPs removal, such as primary and advanced membrane filtration, ozonation, chlorination, flocculation/sedimentation and addition of activated carbon. Different technologies with short characteristics are presented in Table 4.

Experiments with addition of ferric chloride ($FeCl_3$), aluminum sulphate ($Al_2(SO_4)_3$) and aluminum polichloride (PAX-18) were performed to observe the removal rates of ibuprofen, naproxen, diclofenac, carbamazepine, diazepam and two fragrances – tonalide and galaxolide. Only efficient removal of tonalide, galaxolide and diclofenac was observed and efficiency amounted to 50–75 %. Elimination of neutral musks was more effective with addition on PAX-18, while usage of $FeCl_3$ gave better results for diclofenac coagulation (Carballa et al., 2003).

Microfiltration and nanofiltration were investigated for advanced treatment of WWTP effluent. What is more, nanofiltration could be a satisfactory pretreatment process for further water reuse. Additionally, bacteriological tests were performed for the ultrafiltrated effluent and it has been shown that large amounts of pathogens and bacteria were removed. Experiments conducted at Ede WWTP, the Netherlands, indicated more than 95 % removal efficiency of turbidity and solids (Graaf et al., 1999).

Pilot plant supplied with WWTP's effluent for ozonation process, followed by UV disinfection facilities was investigated in order to observe removal of detected pharmaceutical compounds (Ternes et al., 2003). From this work it is concluded that ozonation process is appropriate tool for removal of pharmaceuticals, musks and estrogens, and can inactivate microorganisms at the same time. Furthermore it is expected that advanced oxidation may eliminate pharmaceutical's effects of examined compounds (Ternes et al., 2003). However, it has to be pointed out that occurrence of by-products during this experiment has not been investigated.

In order to study the transformation routes of estrogens in the sewage treatment system, spiked with hormones batch experiments with activated sludge were performed (Ternes et al., 1999b). Based on analytical analysis of hormones, it was assumed that 17α-estradiol was almost quantitatively oxidized to estrone. Furthermore, one of human metabolites, 16α-hydroxyestrone, was not identified as degradation product of estrone and degradation products could not be identified. Another batch experiment with addition of 17α-ethinylestradiol revealed no appreciably elimination for this compound. It appeared that sorption was not a factor in this experiment. Contraceptive mestranol, which hydrolyzes to 17α-ethinylestradiol, indicated its persistence in contact with activated sludge during 24–72 hour test (Ternes et al., 1999b).

An interesting experimental plant bas been built in Australia, including lime clarification, dissolved air flotation, dual media filtration, ozonation, biological activated carbon filtration, microfiltration, combined reverse-osmosis/nanofiltration and UV disinfection units (Khan et al., 2004). The plant was supplied with wastewater effluent. In order to investigate all units with removal efficiency of pharmaceuticals, trial experiments were performed with spiked compounds, respectively. From this study it could be concluded that the most efficient removal was observed for reverse osmosis system. This system was able to demonstrate significant removal of examined compounds including hormones (Khan et al., 2004).

General discussion

Summarizing, there is a strong need for developing a sustainable technology for PPCPs removal from wastewater. From the literature review it can be concluded that the presence of biologically active compounds is confirmed in hundreds of analyzed samples taken from wastewater treatment plants all over the world. Very small concentrations of PPCPs found even in drinking water samples increase the attention not just of researchers but also public opinion. Those small amounts of PPCPs accumulating over the years in water basins may cause harmful effects on aquatic organisms. It has to be pointed out that water is thought as renewable source, which is true only considering regional perspective. Globally, water is circulating in the hydrogeological cycle and it should be taken into consideration that water has it own history and past (Water use and management, 2000). Further investigations should be focused on finding an advanced removal system for small amount of PPPCPs as undertaking of sustainable water management. The main problem with finding the technology for PPCPs removal is not only the small quantities that has to be handled but also the variety of chemical properties of those compounds and different degradation routes.

There is not enough data published considering removal methods and technologies of micropollutants. However, from the available data the highest removal efficiency was obtained for advanced oxidation methods and it seemed to be future treatment system for PPCPs removal (Ternes et al., 2003; Boyd et al., 2005). On the other hand, there is lack of information concerning oxidation by-products, oxidation reaction itself and toxicological risk assessment to provide this technology as a safe one. Treating wastewater treatment plant's effluent with a dosage of ozone or other strong oxidant would be risky without knowing what it contains and without analyzing degradation products.

The most interesting removal system is membrane technology. Separation of micropollutants onto membrane surface gives satisfactory results in experiments. Nanofiltration and reverse osmosis are technologies used for water reclamation and reuse. Reclamation of water gains an increasing attention, not only in areas with water scarcity, like the USA, where water reclamation is performed on large-scale since the early 1970s, but also in countries with satisfactory water resources. Second promising technology is membrane bioreactors system which combines the activated sludge process and replacement for sedimentation at the same time. Another advantage of this system is the possibility of maintaining a long sludge age, which may allow the micropollutants to be degraded into harmless compounds.

Conclusions

- Most of the recent published data concerns identification of PPCPs; presence of pharmaceutical residues in the water and waterwater was confirmed in hundreds of analysed samples around the world
- Analysis of WWTP effluents revealed that exisiting treatment methods are not efficient for PPCPs removal and there is strong need for improvement
- Necessity for gaining the knowledge of PPCPs removal technologies is highly required
- Development of new advanced technologies for pharmaceuticals' removal is needed

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