Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.942559

53 (2015) 2816–2824
March

Taylor & Francis
Taylor & Francis Group

Mechanism of removal of pharmaceuticals and personal care products by nanofiltration membranes

Haiyan Yang*, Xinmiao Wang

Key Laboratory of Urban Stormwater System and Water Environment (Ministry of Education), Beijing University of Civil Engineering and Architecture, Beijing 100044, China, emails: yanghaiyan@bucea.edu.cn (H. Yang), wangxinmiaos@163.com (X. Wang)

Received 16 July 2013; Accepted 18 June 2014

ABSTRACT

Much attention has been paid to pharmaceuticals and personal care products (PPCPs). Nanofiltration (NF) is a new type of separation technology developed between ultrafiltration and reverse osmosis (RO) in the mid-1980s, which is a continuation and development branch of the ultra-low pressure RO technology. PPCPs are a kind of water ubiquitous trace organics, and there are some disadvantages of the PPCPs, such as recalcitrance, accumulation of biological toxicity and long-term dangers, which gradually attracts the attention of the scientific community due to the harm to the environment and ecosystems. This paper analyses the latest research progress in this country and overseas, introducing the advantages on removal of the PPCPs by NF membranes, also recommending the mechanism of the removal process and influencing factors. The direction of future research is proposed as well.

Keywords: PPCPs; Nanofiltration membrane; Water treatment

1. Introduction

To begin with, we will provide a brief background on the pharmaceuticals and personal care products (PPCPs). Over the course of the past decade, the concept of PPCPs has been constantly appearing in a variety of journals, attracting the attention of the majority of the water environment workers [1,2]. The various forms of the PPCPs and their metabolites exist in the environment, which have been generally detected in surface water, groundwater, drinking water, soil and sludge, with the level of ng/L-μg/L, and producing the long-term risks on the water supply, environmental quality and ecosystem security [3,4]. The hidden hazards are not visible in everyday life, so it is necessary to conduct further research and discussion for its complex and ambiguous fate.

This will be followed by a description of the problem and a detailed presentation of how the functions are defined. Nowadays, from a specific reality, with the continuous progress of urbanization, pollution problems will be growing, as well as enhancing the quality of life requirements, so studies are carried out on various continuous accumulations of toxic

*Corresponding author.

Presented at 2013 International Environmental Engineering Conference and Annual Meeting of the Korean Society of Environmental Engineers (IEEC 2013) Seoul, Korea, June 11–13, 2013

micropollutants. With the continuous improvement of the detection technology, most of the trace amounts of PPCPs can be detected by different methods, even degradation or removal [5,6]. As we all know, their concentration is very low, but the cumulative effect of the biological toxicity may be lasting, which can be passed through the food chain, then top predators and even people accumulate the biological toxicity. Moreover, there are many ways for the PPCPs getting into the environment, such as cleaning slate, swimming in human's daily life, then as a result of that personal skin care products directly into the aquatic environment, also enter the water environment in the drug production process, as well as the process of handling expired and unused drugs [7,8], which causes harm to the water environment systems.

1.1. Research status at domestic and overseas

Many research studies have been carried out on this topic. Many types of PPCPs were found in the rivers from the United States Geological Survey (USGS, US Geo) institutions, a variety of PPCPs were discovered in drinking water, in 24 large cities in 2010, comprising 56 types. These PPCPs pollutants discovered may have an impact on human embryonic cells, kidney cells, blood cells and breast cells; some may also cause the phenomenon of the feminization to male fish; even the trace of PPCPs can also be found in a variety of vegetables, especially the vegetables which can be eaten raw, such as lettuce, celery, etc. [9]. In areas with a higher degree of urbanization in China, it has been more common to detect different types of emerging pollutants, including Persistent Organic Pollutants (POPs), Endocrine Disrupting Chemicals (EDCs) and PPCPs in drinking water and sewage. The super pathogenic bacteria are induced by PPCPs, posing a major challenge to the safety of the human society and ecological environment [10].

To attract wide attention at the same time, domestic and overseas scientists conducted numerous removal experiments, determining the impact of factors for many types of PPCPs as well, and achieved certain results. However, conventional water treatment processes cannot effectively remove PPCPs. Details on this are discussed in the following sections.

1.2. Flocculation and coagulation

The studies conducted by Ternes et al. [11] have shown the removal effect of using ferric chloride as a coagulant during coagulation and precipitation test. But the removal effect for five common PPCPs (diclofenac, carbamazepine, clofibric acid, bezafibrate and primidone) is not reaching 10%; Carballa et al. [12] conducted the research, which has shown that the highest removal efficiency of musk is from 50% up to 70% during the flocculation test, while the removal rate of other PPCPs pollutants is less than 25% and almost no carbamazepine and ibuprofen is removed.

1.3. Activated sludge process

Ternes et al. [13] measured adsorption constant of some PPCPs in the primary and secondary sludge, which have explained the removal mechanism. But the *Kd* values of the drugs (diclofenac, clofibrate acid, ibuprofen, ifosfamide and cyclophosphamide) are very low, so sludge adsorption is almost incapable to remove these drugs. However, Song et al. [14] considered that although sludge can absorb PPCPs, the degradation requires sufficient retention time (SRT), in fact, the majority of existing sewage treatment plants design the SRT which is not long enough for degradation of PPCPs at the operational process.

1.4. Advanced oxidation technology

The research conducted by Ternes et al. [15] has indicated that ozone is very effective for removing PPCPs, when adding 0.5 mg/L ozone to raw water, the degradation rate of carbamazepine and diclofenac with the concentration of 1,000 ng/L in the raw water is 97%; and adding 1 mg/L ozone to raw water, the degradation rate of down solid alkyd and oxcarbazepine with the concentration of 1,000 ng/L can reach 50%. Rosal et al. [16] adopted the TiO_2 catalytic ozone method to remove drop solid alkyd at 25℃, which can significantly reduce the consumption amount of ozone and enhance the removal effect. Adding a catalyst with the concentration of 1 g/L, when pH 3, the PPCPs can be removed completely in less than 60 min; while at pH 5, in less than 10 min. The effect of TiO_2 catalytic oxidation is very obvious. Zwiener and Frimmel [17] used O_3/H_2O_2 to oxidize PPCPs, and studied the factors and effects of this method. Further research is needed on universal applicability of treating PPCPs using ozone and chlorine. The TOC removal rate is not high using ozone in PPCPs treatment processing at the same time, yet there are not clear reports on whether it will generate the harmful intermediate byproducts or not.

1.5. Activated carbon adsorption

Nowotny et al. [18] considered the trace PPCPs contaminants of effluent treated by powdered activated carbon (PAC) adsorption process in the city sewage treatment plant, and these pollutants include 10 kinds of medicines, four kinds of developers and eight kinds of industrial compounds. The results show that other drugs except the developer all have good adsorption effect and high removal rate with the PAC dosage of 10 mg/L; and the developer (except diatrizoate acid) concentration was reduced to 1% of its initial concentration with the PAC dosage of 70 mg/L. Boehler et al. [19] conducted the studies that have shown that the sorption of common five kinds of PPCPs (diclofenac, carbamazepine, clofibric acid, bezafibrate and primidome) by PAC, knowing that the removal rate is also high. But activated carbon method's cost to remove PPCPs is higher and PAC adsorption saturation will also have a secondary pollution if not handled properly.

1.6. Membrane technology

Yoon et al. [20] conducted a comparative study of nanofiltration (NF) and ultrafiltration (UF) for the removal of 27 kinds of different PPCPs in water, using of dead-end filtration process. The analysis results show that the NF process is mainly hydrophobic adsorption and filtering repulsion, while the UF process is a hydrophobic effect and the processing efficiency is very low. Radjenović et al. [21] treated the water samples of well water, drinking water, NF and RO desalination water treatment plants through concentrate processing. The results show that the raw water contains about 31 different concentrations ranging from pharmaceutical ingredients in the NF and RO membranes for groundwater rejection, with good retention performance and the removal rate of almost all drugs is greater than 85%. While the negative charge of hypoxanthine and dichlorobenzene is greater than 95%, the positively charged sotalol metoprolol retention rate is greater than 90%. The Giessen municipal sewage treatment plant in Germany [22] applied polyethersulfone (PES) membranes, at 0.7 MPa pressure, which almost entirely removed carbamazepine, dichlorobenzene sulphonamide removal rate also reached 65%. With late beginning in our area, a lot of water environment workers have also achieved some encouraging results after hard efforts, such as NF removal of carbamazepine, antibiotics etc. Huang et al. [23] considered a research on factors of carbamazepine (CBZ) removal from drinking water using NF membranes; it was obvious that aperture can affect CBZ removal, and considered the initial concentration, pH, ionic strength and the water temperature. Fan and Qin et al. [24,25] conducted a study on factors of spiramycin removal by NF membranes. In order to get the optimum operating pressure and the optimum temperature, they did the experiment at different pressure and temperature conditions of NF membranes, at the same time, adsorption experiments showed that spiramycin removal by surface adsorption of NF membranes was not obvious. Cheng et al. [26] used NF membranes to deal with trace steroidal estrogen, which shows that NF technology is an effective method for removal of trace steroidal estrogen, with the average retention rate more than 90% and the best removal conditions: pressure of 0.4 MPa, pH 11, conductivity of 0 mS/cm.

In addition, it is also proposed that NF membranes can remove endocrine disruptors. Hu and Zhang [27] removed endocrine disruptor bisphenol A in water using NF membranes, and proposed a further discussion about the operating conditions and solution properties in the NF membrane performance removal experiments, and analysed the interaction between the film and the contaminant molecules for membrane retention performance. Jin and Liguang [28] proposed a trace research on terephthalate removal by NF membranes, they mainly studied the adsorption and rejection characteristics of phthalates by NF membranes and discussed the test parameters that can affect the retention performance of NF membranes. We may understand the rejection of the NF membrane mechanism deeply, with a positive significance on applying the NF membrane in water micro-contamination treatment.

1.7. Summary

Recent research from domestic and overseas shows that the effect of conventional water treatment methods to remove PPCPs is not obvious and a variety of methods to remove PPCPs (the comparison between PPCPs removal craft) are shown in Table 1. It is unclear that after degradation and transformation of the sludge on the activated sludge method (including a membrane bioreactor), which needs to be studied about migration and fate after oxidation of the degradation products of advanced oxidation technology and photochemical degradation method [29], with the disadvantages, such as too long cycle, low efficiency, complicated operation and high costs, membrane processing technology, the method of physical removal of contaminants is excellent, which has more advantages compared with the activated carbon adsorption (required regeneration process) and the studies conducted by Zhou et al. [30] have shown that all the PPCPs rejection rates are very low when using microfiltration, while only for steroids a higher removal rate

Table 1
Comparison between PPCPs removal techniques

Type of process	Applicable water quality conditions	PPCPs removal effect	Advantages and disadvantages
Common process (coagulation, flocculation)	Better water quality	The removal of most of PPCPs is not obvious	Mature technology, low removal rate
Activated sludge methods	Poor water quality	Most of the PPCPs have a certain role in the rejection	Better adsorption, longer sludge age
Advanced oxidation technology	Better water quality, without impurities	Most of PPCPs can be oxidized into harmless substances	Oxidized completely With by-products
Activated carbon adsorption	Better water quality	Most of PPCPs can play adsorption	Without by-products, higher costs
Membrane Technology	Whether water quality is good or not	Poor removal efficiency of microfiltration and ultrafiltration, while nanofiltration and reverse osmosis Most PPCPs have higher removal rate	Shock load no by-products Presence of membrane fouling

is achieved. UF and microfiltration are commonly used as pretreatment before NF and reverse osmosis (RO). Because the osmotic pressure difference between the NF membrane and separation membrane is generally 0.5–2.0 MPa, they are always called ultra-low pressure RO (low-pressure RO), pulsing with negative charge on the NF membrane and Donnan effect [31], achieving the separation of different ions. NF is a more economical method to remove PPCPs compared with RO, so it needs further exploration and study for understanding the mechanism of NF technology.

2. NF technology

NF is a new type of membrane separation technology which was developed between UF and RO in the mid-1980s (various film performances are shown in Table 2), and it is a continuation and development of the ultra-low pressure RO technology. NF was called a low-pressure RO membrane or loose RO membrane at early time, which is making up for the gap between the RO and UF. NF is becoming an independent technology after separating from the RO technology. The great feature of NF membranes is with a charge itself, which determines that a higher desalination performance in low pressure also can remove dissolved components at a nanometre level.

The NF membrane is a separation membrane with a nanoscale charged microporous structure, in the application process it has two significant characteristics: first, the screening effect [32], retaining small molecular weight objects such as neutral solute organisms and viruses; second, different valence anion has the dual effect of screening and charge (charge effect known as the Donnan effect i.e. the electrostatic interaction of the ions with the membrane), which is the important reason for the NF membrane still having a certain rejection at a very low pressure (as opposed to

Table 2
Various membrane performances

Membrane technology	Driving force	Handle material form	Membrane structure	MWCO	Separation mechanism
MF	Pressure difference (0.01–0.2 MPa)	Liquid or gaseous	Symmetric or asymmetric porous membrane	0.02–10 μm	Screening
UF	Pressure difference (0.1–0.5 MPa)	Liquid	Asymmetric membrane with cortex	Almost 120 μm	Screening
NF	Pressure difference (0.5–2.5 MPa)	Liquid	Densification of asymmetric and composite membranes	More than 1 nm	Solution—diffusion Screening
RO	Pressure difference (1–10 MPa)	Liquid	Densification of asymmetric and composite membranes	0.1–1 nm	Solution—diffusion

the high-pressure RO). So the NF separation technique is "clean" (no by-products). Water treatment process based on a NF membrane may be an ideal alternative to ozone/biological activated carbon [33], with a very promising future in the removal of micropollutants. To ensure the quality of drinking water, it is necessary to further investigate the mechanism of NF removal.

2.1. The main mechanism model of the NF membrane removal of PPCPs

The NF membrane mass transfer mechanism is usually considered as a solution–diffusion model, and the NF separation mechanism is complex for many factors such as the pore size of the NF membrane which is close to the molecular level, the membrane surface charge, particularly the physicochemical properties of the solute (especially small PPCPs), interactions between the membrane and solute, also solute and solute, so there is not a comprehensive explanation for the present NF membrane separation mechanism. The main models of the NF membrane separation mechanism proposed in recent years are non-equilibrium thermodynamics, solution–diffusion model, not completely dissolved diffusion model, pore model, charge model, the electrostatic repulsion and steric hindrance model, the DSPM model and the MS model. The dissolution of the diffusion model and the hybrid model is the typical charge models.

2.2. Pore model

Pore model is based on a friction model of Stokes-Maxwell [34], assuming that the membrane has a uniform pore structure and introducing steric factors. The model considers the two types of membrane pores of the solute passes, including the diffusion flow caused by pressure difference on both sides of the membrane and the convective flow caused by concentration gradients. Taking the possible interactions between the solute and the film hole into account and space steric effect of the solute in the membrane pore [35], the pore model can describe the NF membrane separation mechanism of neutral solute system, fit to the evaluation of the NF membrane structure, so it is widely used for the characterization of the NF membrane structure size and neutral solute separation performance prediction.

2.3. Dissolution–diffusion model

The dissolution–diffusion model assumes that the membrane surface is a non-porous homogeneous state. Solute and solvent are dissolved in the film surface layer at first, and then go through the membrane at respective chemical potential difference. The model is also based on the ideal thermodynamics, the influence of the concentration on the diffusion is negligible, and they are independent of each other for solute solvent passing through the membrane pores [36]. In fact, these assumptions are not valid in the membrane separation process. So the dissolution–diffusion model is only applicable to a model based on a pure diffusion, and cannot be used in a concentration gradient-driven model [37]. Taking this into account, it is necessary to expand the dissolution–diffusion model based on the incomplete dissolution–diffusion model, which is more realistic than the dissolution–diffusion model by increasing the membrane pores of solute solvent convection.

2.4. Hybrid model

Many single models are built in this ideal state, but some assumptions may not be established in a different case and therefore, it is necessary to improve the separation model. Based on the ideal model for the study, in the actual situation, you should analyse the combination of different models. The two typical NF hybrid models are the Daonan-steric model and electrostatic steric hindrance model, while the model of the electrostatic potential barrier is combined with the pore model and the fixed charge model. The Daonan-steric model is similar to the electrostatic steric model in types of the hybrid model, and ions in the finer pores are affected by the steric, so the model is also an important way to understand the mechanism of NF [38]. Polarity (or charged) rejection of solutes through NF membranes is jointly determined by the electrostatic interaction and the steric effect, however, non-polar solutes mainly depends on the steric effect.

2.5. Summary

Consideration the combination of the removal mechanism model of the NF membrane, the main separation mechanism for trace organic compounds (mainly related to PPCPs target material removal) is particle size exclusion, electrostatic repulsion and NF membrane material hydrophobic adsorption. Thereby, the structural features of drugs, the physicochemical properties and the nature of the NF membrane should also be taken into account, since they are important factors affecting PPCPs removal. When organic matter is electrically neutral, the separation mechanism is sieve size exclusion; while organics are negatively charged, mainly steric effects and electrostatic repulsion. So while discussing the removal mechanism, it needs an in-depth research on the factors of PPCPs removal.

3. The influencing factors of PPCPs removal by a NF membrane

3.1. Membrane

Different membrane structures in the process will be influenced by different factors, if molecular weight cut-off (MWCO) is not considered as the main factor, which means that the molecular weight of drugs is less than the membrane MWCO. Normally, the factors of membrane structure characteristics are MWCO of the membrane, salt rejection, porosity, etc. [39,40].

MWCO refers to the molecular weight whose retention rate is 90%, but during the process of separating organics, it is only a rough estimate of the size on the membrane sieving effect using MWCO. The factors that are considered in selecting films are salt rejection and MWCO. The impact is in the affirmative, though there different opinions and opposite results. Porosity is the important parameter of membrane structure, which can be characterized using the pore size and pore size distribution. When the membrane pore size is small and excluding electrostatic interactions with organic, the porous structure of the film is the main parameter, otherwise, it is a minor factor.

3.2. Removal objects

The screening effect is determined by the required removal molecular size and the structural characteristics of the membrane. Molecular weight (MW) is the important parameter at expressing the molecular size, which can be used to predict the uncharged organic molecule removal rate trend [41,42], but MW only quantitatively describes molecules, even having the same MW and different geometric shapes, the effect of the membrane will be different. Therefore, the impact factors are the size of molecules and molecular polarity. Yoon et al. [43] divided 52 kinds of EDCs and PPCPs into two categories in accordance with the physical and chemical properties: one class is polar, less volatile, hydrophilic compounds, finding a NF membrane rejection performance generally in the range of 44–93%, lower rejection rate of this class of compounds. Another class is weakly polar, more volatile, hydrophobic compounds; the rejection of the NF membrane of such compounds is higher than that in the former category. It is believed that the hydrophobic nature of the compound and the molecular size are dominant factors affecting the rejection performance of the NF membrane. So while considering the molecular size and polarity, hydrophobicity must be considered. Comerton and Yoon et al. [44,45] also found that the adsorption between the membrane and drugs is one of the important factors for affecting the removal; most of the high-pressure-driven membrane is hydrophobic, and the size of the hydrophobic membrane surface may be represented by the membrane contact angle, and the larger the contact angle, the more hydrophobic is the membrane.

In addition, the presence of inorganic ions in the solution will affect the removal effect, especially divalent ions such as Ca^{2+}, which is compressing the Debye length or the thickness of the electrical double layer of the surface of the membrane, and neutralizing or weakening the negative charge of the surface of the membrane, so it causes the membrane surface functional groups of the mutual repulsion weakened, to make the membrane pore size smaller. However, different researchers have different views on the ionic strength of the membrane to remove drugs. Kim et al. [46] conducted the studies showing that the solution in the presence of natural organic matter has a significant impact on drugs and other trace organics removal using membrane technology, but other studies are not very consistent. In general, the solution ionic strength also affects the removal of the effect of considering factors.

3.3. The relationship between the film and removal objects

Electrostatic interaction [47,48] is an important mechanism for removing small charged molecule drug by the film, the major charge of the NF membrane surface is negative, the charge is usually represented by the zeta potential. Deshmukh and Childress [49] confirmed that the zeta potential is decreased by increasing the solution pH. When pH is above the isoelectric point, the charge of the membrane is positive, or else negative, because the functional group of the film gets a proton. The solution pH also affects the nature of the organic molecules, because the functional group of the organic molecules ionization state is related with the pH and an acid dissociation constant pKa. At a certain pH, a different charge is produced by a different pKa due to the different structures of the drugs (such as sulfamethoxazole presents two pKa, which are 1.7 and 5.6, respectively. When the $pH < 1.7$, the charge is positive, $1.7 < pH < 5.7$, neutral, $pH > 5.7$, negative [50]). Thus, the electrostatic repulsion or electrostatic attraction is generated between the antistatic film and drug. Kimura et al. [51] conducted the removal test of nine organic compounds, including drugs, using NF and RO membranes. The results showed that the physical and chemical properties are different between films and organics. The removal of five negatively charged organics was significantly higher than the other four organics uncharged, which led to electrostatic repulsion of the film. However, there are few studies conducted to show the impact on the removal rate for the electrostatic attraction between positively charged organic compounds and the negatively charged membrane. Verliefde et al. [52] observed that the concentration of positively charged membrane surface is increased by the electrostatic attraction, making the removal rate decrease. So it is necessary to take a key consideration for this action.

Zhao and Jia [53] showed that the pH of water body can change the membrane surface charge. The pH will change the charge nature of the membrane surface and pore size, which also can affect the interaction of the solutes and the membrane by changing the solute existence form, so pH may have an important impact on the film materials and its water flux. This hot topic as attracted international attention for the complicated mechanism. The studies conducted by Pan et al. [54] showed that increasing pH might lead to deprotonation of the membrane surface functional groups, and then the negative charge of the surface of the film is increasing. When the pH of the water is greater than the acid ionization constant pKa of the drug (PPCPs), organics (PPCPs) ionization is with negative electricity, so generating electrostatic repulsion in the negatively charged surface of NF membrane and the removal of organics (PPCPs) is improved.

3.4. Summary

The various factors affecting the removal process may be interacting and interdependent, so the removal rate may be opposite in different circumstances. In addition, the membrane mass transfer and separation mechanism is not systematic and in-depth, which can lead to incomplete and not meticulous interpretation of the test results. Therefore, it is necessary for the removal mechanism and influence factors unremitting exploration to make more scientific explanation in each removal process, so as to play a more effective and efficient role in guiding the future work and learning.

4. Conclusion and outlook

Relative to traditional removal processes, retention effect of the relative molecular mass 150–1,000 PPCPs by the NF technology is better [55,56]. The use of the NF membrane process can not only greatly improve water quality, protect drinking water for human health, but it can also greatly save floor space and land acquisition costs and reduce investment in infrastructure [57]. With the NF technology evolving, while the membrane cost is reducing and the membrane pollution control technology is innovatory, we believe that NF technology will play a pivotal role in China's ecological civilization construction and economic development, also improving our country's water industry treatment level. There are many areas which need to be improved for NF membranes, for example, perfecting membrane mass transfer mechanism, enhancing antioxidant and antipollution ability. It is necessary to ensure that the water meets the requirements of the NF membrane separation by conducting raw water pretreatment, thereby, reducing membrane fouling and extending membrane life, optimizing online automated detection technology, etc. The NF membrane technology in water treatment and other areas is bound to have a broader development prospect [58].

References

[1] C.G. Daughton, T.A. Ternes, Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environ. Health Perspect. 107 (1999) 907–938.
[2] Hu Hongying, Cao Wang, Meiting Guo, Status and progress of pharmaceuticals and personal care products (PPCPs) environmental pollution, Ecol. Environ. 14(6) (2005) 947–952.
[3] P. Wang, T. Yuan, Y. Tan, Research progress of drug contamination in the water environment and migration and transformation behavior, Environ. Sci. Technol. 31(9) (2008) 57–61.
[4] Y. Tang, N. Gao, W. Pang, Q. Li, Drugs and personal care products in the current situation in the water environment and removal, Water Supply Drainage 34 (6) (2008) 116–121.
[5] P. Westerhoff, Y. Yoon, S. Snyder, W. Eric, Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes, Environ. Sci. Technol. 39 (2005) 6649–6663.
[6] N. Nakada, H. Shinohara, A. Murata, K. Kiri, S. Managaki, N. Sato, H. Takada, Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant, Water Res. 41 (2007) 4373–4382.
[7] O.A.H. Jones, N. Voulvoulis, Human pharmaceuticals in wastewater treatment processes, Environ. Sci. Technol. 35 (2005) 401–427.
[8] M. Carballa, F. Omil, J.M. Lema, Removal of cosmetic ingredientsand pharmaceuticals in sewage primary treatment, Water Res. 39(19) (2005) 4790–4796.

[9] X. Wu, J.L. Conkle, J. Gan, Multi-residue determination of pharmaceutical and personal care products in vegetables, J. Chromatogr. A 1254 (2012) 78–86.

[10] X. Zhang, Nanophase drinking water and wastewater treatment processes change, Water Supply Drainage 38(4) (2012) 1–67.

[11] T.A. Ternes, M. Meisenheimer, D. Mcdowell, F. Sacher, H.J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert, Removal of pharmaceuticals during drinking water treatment, Environ. Sci. Technol. 36 (2002) 3855–3863.

[12] M. Carballa, F. Omil, J.M. Lema, Removal of cosmetic ingredients and pharmaceuticals in sewage primary treatment, Water Res. 39(19) (2005) 4790–4796.

[13] T.A. Ternes, N. Herrmann, M. Bonerz, T. Knacker, H. Siegrist, A. Joss, A rapid method to measure the solid–water distribution coefficient (Kd) for pharmaceuticals and musk fragrances in sewage sludge, Water Res. 38(19) (2004) 4075–4084.

[14] C. Song, C. Wang, H. Li, Several mechanism for removing drugs and personal care products in wastewater treatment and comparison, J. Environ. Eng. 3 (11) (2009) 1921–1930.

[15] T.A. Ternes, M. Meisenheimer, D. McDowell, F. Sacher, H. J. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme, N. Zulei-Seibert, Removal of pharmaceuticals during drinking water treatment, Environ. Sci. Technol. 36(17) (2002) 3855–3863.

[16] R. Rosal, M.S. Gonzalo, A. Rodríguez, E. García-Calvo, Ozonation of clofibric acid catalyzed by titanium dioxide, J. Hazard. Mater. 169(1–3) (2009) 411–418.

[17] C. Zwiener, F.H. Frimmel, Oxidative treatment of pharmaceuticals in water, Water Res. 34(6) (2000) 1881–1885.

[18] N. Nowotny, B. Epp, C. Von Sonntag, H. Fahlenkamp, Quantification andmodeling of the elimination behavior of cologically problematic wastewater micropollutants by adsorption on powdered and granulated activated carbon, Environ. Sci. Technol. 41(6) (2007) 2050–2055.

[19] M. Boehler, B. Zwickenpflug, J. Hollender, A. Joss, H. Siegrist, Removal of micropollutants in municipal wastewater treatment plants by powder-activated carbon, Water Sci. Technol. 66(10) (2012) 2115–2121.

[20] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, J. Yoon, Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes, Desalination 202 (2007) 16–23.

[21] J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, Water Res. 42 (2008) 3601–3610.

[22] M. Röhricht, J. Krisam, U. Weise, Elimination of pharmaceuticals from wastewater by submerged nanofiltration plate modules, Desalination 250 (2010) 1025–1026.

[23] Y. Huang, H. Zhang, B. Dong, Nanofiltration membrane to remove the impact of factors of carbamazepine.Environmental, Science 32(3) (2011) 705–710.

[24] W. Fan, P. Qin, Nanofiltration Antibiotics in Water, Beijing University of Chemical Technology, Beijing, 2012, pp. 73–74.

[25] L. Wang, X. Zhu, J. Wang, Z. Tian, The antibiotic residues and potential risk of environmental water, Ind. Water Treat. 29(5) (2009) 10–13.

[26] A. Cheng, L. Wang, X. Wang, H. Zhang, L. Zhang, R. Zhang, Z. Wang, Nanofiltration membrane removal trace steroidal estrogen, Membr. Sci. Technol. 28(5) (2008) 90–93.

[27] J. Hu, Y. Zhang, The Research of Nanofiltration Membrane to Remove Water Endocrine Disruptor Bisphenol A, Shenyang Normal, Shenyang, 2011, pp. 6–15.

[28] Y. Jin, W. Liguang, The Study of Nanofiltration Membrane Removal of Trace Phthalates, Technology and Business University of Zhejiang, Zhejiang, 2011, pp. 9–16.

[29] S.A. Snyder, Samer Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, E.C. Wert, Y. Yoon, Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, Desalination 202(1–3) (2007) 156–181.

[30] X. Zhou, Y. Zhang, C. Dai, Drugs and personal care products (PPCPs) in drinking water removal characteristics of study progress, J. Environ. Health 11(25) (2008) 1024–1027.

[31] Y. Sanchuan, C. Gao, H. Zhang, Nanofiltration membrane technology and micro-polluted water treatment, Water Treat. Technol. 31(9) (2005) 6–9.

[32] W. Shunze, B. Wang, Charged nanofiltration membrane separation of organics, Water Treat. Technol. 26 (5) (2000) 249–252.

[33] Yu Shuili, Drinking water treatment technology based on the nanofiltration membrane technology, Water Ind. Market 7 (2012) 23–25.

[34] S. Nakao, S. Kimura, Models of membrane transport phenomena and their applications for ultrafiltration data, J. Chem. Eng. Jpn. 15 (1982) 200–205.

[35] X. Wang, Nanofiltration membrane mechanism and application research progress, Chem. Bull. 2 (2001) 86–90.

[36] S. Qiu, W. Liguang, L. Zhang, C. Huanlin, G. Congjie, The mechanism of nanofiltration membrane technology, Water Treat. Technol. 35(1) (2009) 15–19.

[37] H. Mehdizadeh, K. Molaieenejad, Modeling of mass transport of aqueous solutions of multi-solute organics through reverse osmosis membranes in case of solute–membrane affinity. Part 1: Model development and simulation, J. Membr. Sci. 267 (2005) 27–40.

[38] X. Wang, Nanofiltration membrane mechanism and application research progress, Chem. Bull. 2 (2001) 86–90.

[39] B. Van der Bruggen, J. Schaep, D. Wilms, C. Vandecasteele, Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration, J. Membr. Sci. 156 (1999) 29–41.

[40] B. Van der Bruggen, C. Vandecasteele, Modelling of the retention of uncharged molecules with nanofiltration, Water Res. 36(5) (2002) 1360–1368.

[41] K. Kimura, G. Amy, J.E. Drewes, Y. Watanabe, Adsorption of hydrophobic compounds onto NF/RO membranes: An artifact leading to overestimation of rejection, J. Membr. Sci. 221 (2003) 89–101.

[42] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment-a literature review, Water Res. 38 (2004) 2795–2809.

[43] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products, J. Membr. Sci. 270(1–2) (2006) 88–100.
[44] A.M. Comerton, R.C. Andrews, D.M. Bagley, P. Yang, Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds, J. Membr. Sci. 303 (2007) 267–277.
[45] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, J. Yoon, Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes, Desalination 202 (2007) 16–23.
[46] D.H. Kim, H.K. Shon, G. Sharma, J. Cho, Charge effect of natural organic matter for ultrafiltration and nanofiltration membranes, J. Ind. Eng. Chem. 17 (2011) 109–113.
[47] X.L. Wang, W.N. Wang, D.X. Wang, Experimental investigation on separation performance of nanofiltration membranes for inorganic electrolyte solutions, Desalination 145 (2002) 115–122.
[48] X.L. Wang, T. Tsuru, S. Nakao, S. Kimura, The electrostatic and steric-hindrance model for the transport of charged solutes through nanofiltration membranes, J. Membr. Sci. 135 (1997) 19–32.
[49] S.S. Deshmukh, A.E. Childress, Zeta potential of commercial RO membranes:influence of source water type and chemistry, Desalination 140 (2001) 87–95.
[50] M. Ge, X. Li, X. Zeng, Q. Zhu, The research progress of nanofiltration theory, Fluid Mach. 35(1) (2005) 35–39.
[51] K. Kimura, S. Toshima, G. Amy, Y. Watanabe, Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes, J. Membr. Sci. 245 (2004) 71–78.
[52] A.R.D. Verliefde, E.R. Cornelissen, S.G.J. Heijman, J.Q.J.C. Verberk, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, The role of electrostatic interactions on the rejection of organic solutes in aqueous solutions with nanofiltration, J. Membr. Sci. 322 (2008) 52–66.
[53] K. Zhao, J. Jia, Dielectric analysis of multi-layer structure of nanofiltration membrane in electrolyte solutions: Ion penetrability, selectivity, and influence of pH, J. Colloid Interface Sci. 386 (2012) 16–27.
[54] S. Pan, J. Qiu, Y. Zhou, C. Gao, The RO/NF membrane mass transfer progress affected by pH, Water Treat. Technol. 37(4) (2011) 4–9.
[55] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Pharmaceutical Retention Mechanisms by Nanofiltration Membranes, Environ. Sci. Technol. 39(19) (2005) 7698–7705.
[56] T. Qiao, X. Zhang, O. Huiting, Research progress of pharmaceuticals and personal care products in drinking water, Water Supply Drainage 36(4) (2010) 118–125.
[57] J. Zhou, B. Dong, PPCP's research progress removal of nanofiltration membrane in drinking water, Water Supply Drainage, 35(z) (2009) 13–17.
[58] Y. Yang, Nanofiltration membrane technology research and market progress, Inform. Rec. Mater. 12 (6) (2011) 41–49.