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Evaluation of membranes as promising technique for reclamation and reuse of wastewater

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Abstract: In 21st century water is a precious resource and after the emphasis on the water sustainability, its proved to be a challenge for water treatment systems to treat wastewater good enough to make it reusable for different purposes. Studies around the world reported the presence of many organic micropollutants like pharmaceuticals and pesticides in the water treated with conventional treatment processes. These micropollutants pose a serious threat towards the aquatic environment especially in case of antibiotic resistances bacteria. Advance treatment processes are one of the most discussed methods to minimize this treat. But rapid expansion of the population in developing countries caused the existing conventional wastewater treatments plants overloaded and there will be no space available for expansion of the existing treatment plants. This leads towards an attractive option of membrane technology. Plenty of membrane designs and operational setups are available in the market. Efficiencies of membrane technology differs with the types of targeted pollutants presents in wastewater and type of membrane being used. The scope of present study covers the types, mechanisms and constraints of the membrane systems to treat wastewaters for pharmaceuticals. A short review has been presented in which reliability on Nanofiltration is discussed with respect to pharmaceutical removals. It was noticed that drugs can be successfully treated by using NF coupled with other advance treatment methods.

Key words: Membrane Technology, wastewater reuse, Nanofiltration, pharmaceuticals, micropollutants

1. INTRODUCTION

Wastewater treatment with membrane technology is not a new concept. Different types of membranes are used for the rejection of pollutants around the word. However, efficiency of membranes is strictly dependent on type of membrane and the nature of pollutant (Alturki et al., 2010). Therefore, selection of membrane according to the properties of pollutant is very crucial to avoid membrane fouling and to secure economic losses. Pharmaceuticals are chemical compounds of concern in recent year because of their regular appearances in fresh water resources and drinking water. Although detected pharmaceuticals are in the range of μg/L – ng/L but their impacts are many folds for both aquatic life and humans (Mompelat et al., 2009). Membranes are an attractive technique because of their selective selection property. They restrict the passage of pollutants and make reclaimed water reusable.

Membrane processes are becoming prominent in wastewater reclamation/reuse and drinking water treatments due to their effectiveness in removing both organic macro, micro and micropollutants. Membranes are divided in MF (Microfiltration), UF (Ultrafiltration), NF (Nanofiltration) and RO (Reverse Osmosis) based on pore size. Pharmaceuticals are treated by membrane technology and in this attempt, studies have published very diversified results regarding efficiency. All of membranes are not effective for all the pharmaceuticals. Membrane rejection is strictly dependent upon water chemistry, drug chemistry and membrane characteristics (Alygizakis et al., 2016).

1.1 Nanofiltration

Nanofiltration (NF) is covered by many studies, particularly for the removal of micropollutants

(Verliefde, 2009; Yangali Quintanilla, 2010). However, these studies were conducted mainly with target compounds spiked in synthetic model water or directly in demineralized water.

NF (0.001µm pore size) and RO are considered to be in same group due to similar characteristics of membrane material, solute removal and transport (Yoon and Lueptow, 2005) but NF has advantage of low operating pressure compared to RO and has high rejection of organic compounds rather than UF. Although only Nanofiltration/Reverse Osmosis (NF/RO) has been reported to be efficient for removal of Pharmaceutically active compounds (PhACs) and other dissolved contaminants from wastewater because the size and molecular weight (MW) of most PhACs are smaller than the molecular weight cutoff (MWCO) of most microfiltration (MF) and ultra-filtration (UF) membranes but RO is still not applicable in every country and in every situation because of its high economic values (Comerton et al., 2009).

Both charge and size are important in NF rejection as at a neutral pH most NF membranes are negatively charged at lower pH it is positively charged. Physical sieving is the dominant rejection mechanism for the colloids and large molecules, however for ions and lower MW organics, chemical interactions between the solutes and membrane can play an important role in rejection mechanism. Characteristics of Nanofiltration along with advantages and disadvantages are given in Table 1.

Table 1. Characteristics of Nanofiltration and advantages and disadvantages

NF Characteristics	Advantages	Disadvantages
Membrane Finely porous/asymmetric composite	Very compact system low liquid holdup	Can be fouled with particulates
Transfer mechanism Sieving, electrostatic hydration/diffusive	Low capital cost	Not good for viscous material
Law governing transfer Fick's law	Back flushable	Limited range of products
Typical solution treatments Ions, small molecules	High packing density	Higher fouling tendency
Typical pure water flux (L/m_2h) 20-200	Lower investment cost	-
Pressure requirement (atm) 7-30	Lower operating cost	-

The aim of this study was to investigate evaluate and demonstrate the effective treatment of pharmaceuticals with Nanofiltration because of it property of multiple treatment mechanism, a low-pressure and relatively low fouling makes NF membrane a promising technique.

2. MATERIAL AND METHODS

For the present study three drugs has been selected i.e. Ibuprofen, Diclofenac and Paracetamol from the group of non-steroidal anti-inflammatory drugs on the bases of their frequent detection from waters, high consumption, low biodegradability, polarity and their adverse impacts on the environments. Among the most consumed non-steroidal anti-inflammatory drugs frequently found in aquatic environments are aspirin, ibuprofen, naproxen and diclofenac and Paracetamol (Fent et al., 2006). Physicochemical and other properties of selected pharmaceuticals are given in table 2. A short review was performed in order to get a close idea about the efficiency of Nanofiltration regarding the treatment of these selected pharmaceuticals.

3. RESULTS AND DISCUSSIONS

In the literature, there are very few NF studies on PhAC removal from drinking water and surface water (Radjenović et al., 2008) because of Nanofiltration mechanism is still not completely studied for pharmaceuticals. But in some cases, high and broad pharmaceutical removal efficiencies are reported with zero by-products formation and without farther disinfection units (Joss et al., 2008) but cost and energy requirements are still an important issue. A short review of selected drugs of concern regarding their rejection by Nanofiltration is given in table 3 to understand the relationship between chemistry of drug and method.

Table 2. Properties and occurrence of selected pharmaceuticals (Nonsteroidal anti-inflammatory drug (NSAID)) in waters. (Padhye et al., 2011; Feng et al., 2013; Albero et al., 2014; Ding et al., 2011)

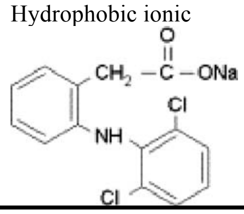
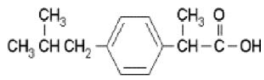
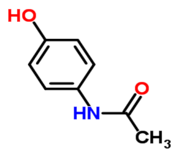
Compound	**Diclofenac**	**Ibuprofen**	**Paracetamol (Acetaminophen)**
Class	Analgesic/ Nonsteroidal anti-inflammatory drug (NSAID)	Analgesic/ Nonsteroidal anti-inflammatory drug (NSAID)	Analgesics/ Nonsteroidal anti-inflammatory drug (NSAID)
Formula	$C_{14}H_{11}C_{12}NO_2$	$C_{13}H_{18}O_2$	C_8H_9NO
Molecular weight [g/mol]	296.15	206.29	151.16
Solubility (mg/L	2/2.37	21	1.40×10^4
Log *K*ow (octanol-water coefficient)	4.26/4.51	3.84/3.97	0.46-0.49
pKa (acid dissociation coefficient)	4.15	4.52/4.91	9.86/9.38
Nature	Hydrophobic ionic	Hydrophobic ionic	Hydrophilic nonionic
Structure			

Table 3. Rejection of pharmaceuticals by Nanofiltration

Diclofenac		**Ibuprofen**		**Paracetamol (Acetaminophen)**	
% Rejection	**Reference**	**% Rejection**	**Reference**	**% Rejection**	**Reference**
≤10	Yoon et al., 2007	55-61	Vergili, 2013	22-78	Yangali-Quintanilla et al., 2010
60	Vergili, 2013	85 - 97	Yangali-Quintanilla et al., 2010	≤10	Yoon et al., 2007
60	Yangali-Quintanilla, et al., 2011	15	Yoon et al., 2007	100	Alturki et al., 2010
85	Alturki et al., 2010	≥95	Alturki et al., 2010	43	Radjenović et al., 2008
100	Radjenović et al., 2008	100	Bellona & Drewes, 2007	*BDL	Bellona & Drewes (2007).
53	Bellona & Drewes, 2007	88	Verliefde, et al., 2009		
*BDL	Kimura et al., 2003				
89	Verliefde et al., 2009				

**BDL=Below Detection Limit*

3.1 Mechanism of Nanofiltration

It is to be noted while performing experiments with NF different mechanisms of solute rejection occur, and each of those mechanisms is influenced by solute, as well as membrane parameters (Asano et al., 2007). Also, feed water composition and operating parameters have an influence on rejection. Three different interaction types are differentiated: size exclusion by steric hindrance, electrostatic interactions and adsorptive interactions (Yangali Quintanilla, 2010)

3.1.1 The molecular weight cut-off (MWCO)

The molar mass above which more than 90% of the compounds are rejected by Nanofiltration membranes is situated in the range of 200-500 g/mol, which corresponds to the molar mass of the organic micropollutants in the source waters for drinking water (mostly surface water, groundwater or riverbank filtrate). Rejection of uncharged or neutral solutes in Nanofiltration often increases with increasing solute molar mass. If the molar mass of an uncharged compound is higher than the MWCO of the membrane, rejection of the compound will usually be high. Molecular size of a compound can be compared to theoretical values for the membrane pore size (Verliefde, 2009)

3.1.2 Polarity Charge on the PhACs

Polarity is also an important parameter to describe rejection in Nanofiltration. Uncharged compounds with a molecular size larger than the pore size of the membrane will be well rejected due to the sieving effect of the membrane polymer network. Polarity can be defined in two ways; Van der Bruggen et al. (1999) described the effect of the permanent dipole moment on rejection. Solutes with a high dipole moment are assumed to be aligned in the direction of the pores of the membrane, due to electrostatic interactions with the membrane charge, which causes the solutes to permeate more easily and thus have a lower rejection (Yangali Quintanilla, 2010). Rejection of charged solutes is dependent on charge repulsions/attractions between the solute and the charged membrane surface. For a negatively charged membrane, charge attractions cause an increase of solute concentration at the membrane surface for positively charged solutes and a decrease of solute concentration at the membrane surface for negatively charged solutes. Rejection of uncharged solutes is mainly dependent on solute size and hydrophobicity (Verliefde, 2009).

3.1.3 Hydrophobicity

Hydrophobic interactions between solute and membrane can cause adsorption of the solute on the membrane surface and in the membrane pores. The higher the hydrophobicity of a compound (expressed by the octanol water partitioning coefficient (log Kow)), the higher the expected adsorption on the membrane. Rejection of hydrophobic solutes is lower compared with hydrophilic solutes of similar size: solute transport increases due to hydrophobic interactions between the solute and the membrane. The more hydrophobic the solute, the larger the influence of hydrophobic interactions on solute rejection. Rejection of hydrophilic solutes is mainly dependent on size exclusion between the solute and the membrane matrix (Verliefde, 2009).

3.1.4 Adsorption

Adsorption on the membrane causes a high initial rejection of the solute. Solution of a solute in the membrane (partitioning) and diffusion through the membrane are important transport mechanisms in membrane filtration processes. It can be expected theoretically, that the more a compound adsorbs on the membrane, the easier it will dissolve into the membrane and thus be transported to the permeate side. A higher log Kow-value (i.e. a higher hydrophobicity) should thus lead to a higher transport of solute and a lower rejection. Initial adsorption of hydrophobic molecules will be high, which causes a high initial rejection, which eventually will drop to an equilibrium concentration when breakthrough is observed (Braghetta et al., 1997).

4. CONCLUSION

A very limited set of publications are available that reported rejection of pharmaceuticals with the help of Nanofiltration. Cost benefit analysis should be conducted regarding pharmaceuticals removal and membrane application in normal wastewater treatment plants.

It was reported that hydrophilic trace organic compounds are effectively removed by NF Membranes but in the case of acetaminophen the retention was observed to be low (i.e., 0, 23,44 %), probably due to its small molecular size (i.e., MW < MWCO). The highest rejections in NF processes were recorded for negatively charged pharmaceuticals diclofenac (95%) and Ibuprofen

(≥ 95). In some literature, negatively charged pharmaceuticals also showed poor removal for which no explanation was found. That means there is still a huge gap in research. Finally, positively charged pharmaceuticals are assumed to have good removal above 90% according to NF mechanism but further research is required. The study proved NF membranes to be very efficient in removing nearly all the pharmaceutical residues. However, after carefully reviewing literature it was observed that sometimes process combinations (membrane-hybrid process) give more than 95% removal of selected drugs. Nano membrane filtration with other technique can achieve an enhanced removal efficiency of a wide range of trace organic contaminants that they alone can't achieve in case of some drugs.

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