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ABSTRACT

Nanofiltration is a promising solution for the removal of emerging and persistent micropollutants, but it is limited by operating expenses due to high membrane areas and operational pressures, dictated by the membrane's low molecular weight cut-offs (MWCO), and the formation of large amounts of concentrate to be treated, e.g. by advanced oxidation. In this paper, a simple solution is proposed to enhance membrane retention of micropollutants by adding cyclodextrins (CDs) for complexation. Complexation between micropollutants and hydroxypropyl β-CD resulted in higher rejections of ibuprofen (99.3%), bisphenol A (94.5%) and phenol (76.4%) compared to filtrations without addition of CDs (82.4%, 14% and 4%, respectively) using a 1 kDa MWCO membrane. The CD complexation allowed for filtration with ultrafiltration (UF) membranes, where nanofiltration (NF) membranes would normally be the best available membrane to retain the micropollutants. By complexation with β-CD polymers, retentions of IBU of 97.0 were even achieved using a 5 kDa MWCO membrane. Operation of larger MWCO membranes will potentially lead to less retentate formation, i.e. higher concentration factors as well as higher operational flux which results in lower membrane area and lower operational expenses. Therefore, the addition of CDs fixated on larger compounds (particles or polymers) may be an efficient and simple solution to increase micropollutant rejection and increase water recovery, while potentially reducing operational treatment expenses. This is of high significance, as it can serve as a simple way to polish contaminated waters by removing micropollutants in large scale wastewater treatment.

1. Introduction

Micropollutant contamination of natural and drinking water from municipal and industrial wastewaters is of increasing concern, as they, even in low concentrations (ng/L–µg/L) have negative environmental impacts (Valbonesi et al., 2021). The micropollutants count everyday products like pharmaceuticals, pesticides, hormones, cosmetics, and other organic compounds. These are not efficiently removed by conventional water (e.g. coagulation combined with sand- or ultrafiltration) and wastewater treatment (e.g. biological degradation) as they are not designed to remove these low-

concentration, highly persistent compounds (Werber et al., 2016; Schwarzenbach et al., 2006). The result is an elevated risk of antibiotic-resistance, bioaccumulation, chronic and acute toxicity, endocrine disruption, and irreversible soil pollution and saturation (de Ilurdoz et al., 2022; Fonseca Couto et al., 2018; Racar et al., 2020). Therefore, there is a great focus on the development of new, efficient technologies for micropollutant removal from these wastewaters.

The first regulation for the removal of these micropollutants from wastewaters can be found in Switzerland, which dictates a micropollutant removal rate of 80% at their urban wastewater treatment plants (Federal Office for the Environment FOEN Water Division, 2019). Nanofiltration (NF) shows rejections of > 80% of many micropollutants (Xu et al., 2020), hence it is efficient to recover these compounds to form a concentrate for further treatment by advanced oxidation processes (AOPs), e.g. photo-Fenton and electro-oxidation, which are more efficient at higher concentrations (Asfaha et al., 2021; Rezende Moreira et al., 2022; Janowska et al., 2020, 2021). Other membrane materials have also shown efficient in removal of micropollutants, dyes and other persistent organic pollutants, e.g. biomimetic membranes and forward osmosis (FO) and reverse osmosis membranes (Chen et al., 2019; Pathak et al., 2018). With osmotic membranes, there is no selection between micropollutants and salts, which will accumulate to form a highly osmotic retentate, which limits the concentration factor. There are two main types of NF membrane materials, the relatively inexpensive polymeric membranes, and the more expensive ceramic membranes, both coming with their specific physicochemical properties and separation mechanisms of the Donnan effect, size exclusion, and solution-diffusion, e.g. the pore size and morphology, pH, surface and molecular charge, hydrophilicity, and concentration. Operational parameters, e.g. temperature, pressure, and flow rate also play a major role when applying this membrane technology (Kim et al., 2022; Schäfer and Fane, 2021). NF is generally considered to be a better economical solution compared to RO, as it operates at lower pressures, resulting in lower operational and maintenance expenses (Pasqualin et al., 2022). However, NF on its turn is limited by the lower permeability of NF membranes compared to e.g. ultrafiltration (UF) membranes, requiring more membrane area, hence higher capital and operational expenses. In addition, the buildup of osmotic pressure of retained compounds in NF limits the concentration factor, resulting in large volumes of retentate to be treated by oxidation processes (Janowska et al., 2021). Finally, NF shows low rejection of some small, hydrophobic compounds, e.g. phenols.

One promising strategy to improve NF rejection of small hydrophobic solutes is membrane functionalization by cyclodextrins (CDs). CDs can form host-guest complexes with numerous substances. CDs are rings of glucopyranose units, mainly 6, 7 and 8 units, i.e. α-, β- and γ-CDs, respectively. CDs are produced by enzymatic degradation of starch by CD glycosyltransferase. Different studies have presented how thin film composite NF membranes can be functionalized with CDs. They found that the functionalization increased water permeability while improving rejection of organic solutes, e.g. dye molecules, due to the formation of an inclusion complex (Liu et al., 2021; Xue et al., 2019, 2020; Li et al., 2021). The cavity of the ring structured CDs is hydrophobic compared to the surrounding water, hence, hydrophobic or less hydrophilic micropollutants will enter the cavity of CDs to

form an inclusion complex. Liu et al. (2021) found that the rejection of reactive brilliant red X-3B was increased from 69% to above 98% when comparing a polyethersulfone (PES) NF membrane with a PES membrane functionalized with β-CDs. In addition, the CD functionalization offers a separation of small organic pollutants from salts, as the CD-functionalized NF membranes have a low retention towards ions compared to small organic molecules (Li et al., 2021). Therefore, there is less buildup of osmotic pressure in NF retentate, allowing for higher concentration factors of pollutants. Membranes have even been functionalized with CDs for selective organic solvent NF (Huang et al., 2020; Xu et al., 2019), and for 99% recovery of acetic acid from dilute solutions (Baruah and Hazarika, 2014). Over time, the capacity of the CD functionalized membranes will be reached and should be regenerated.

In this study, an alternative use of CDs for high rejection and recovery of micropollutants is studied. Instead of functionalization of membranes, CDs will be added to the solutions of micropollutants in excess, to ensure complex formation. Two types of CDs will be studied: Kleptose hydroxypropyl β-CD (HP-β-CD) with a molecular weight of 1501 Da and a β-CD polymer with a molecular weight between 2000 and 300,000 Da. These will potentially allow for separation with UF membranes, which will be studied by filtrations of solutions of ibuprofen (IBU), bisphenol A (BPA) and phenol with 1000, 5000 and 10,000 Da molecular weight cut-off (MWCO) membranes and comparing the performances of these with a standard NF90 membrane (MWCO 200–400 Da). UF membranes will potentially allow for higher permeate fluxes, higher water recovery, less production of retentate and lower operating expenses. In addition, the solution proposed in this study does not require regeneration of membranes capacity towards micropollutants, but addition of more CD, which are low cost with high efficiency of micropollutant complexation. Therefore, it is not necessary to regenerate the CD's as other methods require, e.g. activated carbon technology.

2. Materials and methods

2.1. Preparation of solutions

The complexation between CD host molecules and three guest pollutants and associated retention by membrane filtration were studied. For this, mixtures with and without host molecules were prepared. The guest pollutants were IBU (Na-Ibuprofen salt, M_W 228.3 Da, Sigma Aldrich, IN), Phenol (M_w 94.1 g/mol, Bie & Berntsen, DK) and Bisphenol A (BPA, M_w 228.3 g/mol, Sigma Aldrich, TW). Aqueous solutions with 10 mg/L concentrations of the three pollutants were prepared with and without CDs. Such high concentration was selected for an easier evaluation of the results by HPLC/UV, considering that high rejection and recovery of micropollutants would be disfavored at high concentration and therefore the results presented in this study would be conservative. High rejection and recovery of micropollutants would be higher when working in the ng-µg/L For all three pollutants, inclusion complexes were formed by addition of Kleptose® hydroxypropyl β-CD (HP-β-CD, M_w 1501 Da, Oral grade, Roquette). For IBU, inclusion complexes were also formed by addition of β-CD polymer (Mw 2000–300,000 Da, 60% iodometric CD content, Merck) to 10 mg/L IBU solutions. CDs were

Table 1 – Overview of filtration experiments without CD addition (w/o) and with addition of HP-β-CD and β-CD polymer carried out by filtration of different pollutants with different membranes.

Pollutant	NF90	1 kDa RC	5 kDa RC	10 kDa ETNA
IBU	w/o CD	w/o CD	w/o CD	w/o CD
	HP-β-CD	HP-β-CD	HP-β-CD	HP-β-CD
		β-CD polymer	β-CD polymer	
Phenol		w/o CD	w/o CD	
		HP-β-CD	HP-β-CD	
BPA		w/o CD	w/o CD	
		HP-β-CD	HP-β-CD	

Table 2 – Binding constants for inclusion complexes between IBU, BPA and phenol guest molecules and HP-β-CD and β-CD polymer host molecules. *Measured with ITC. #from Ref. Cai et al. (2020) for HP-β-CD with high degree of substitution.

Pollutant	$K_{1:1}$ (M^{-1}) HP-β-CD	$K_{1:1}$ (M^{-1}) β-CD polymer
IBU*	3584	1908
BPA# (Cai et al., 2020)	14,940	
Phenol*	122	125

added to reach a 10 times higher molar amount of CD than aqueous pollutants.

2.2. Filtration experiments

Solutions of pollutants with and without CDs were filtered in a stirred dead end filtration cell (Solvent-resistant Stirred Cell, XFUF07601, Millipore, MA). The transmembrane pressure (TMP) was adjusted to 5 bar by pressurizing the feed chamber with Nitrogen. The pollutants retention by four membranes was studied; a NF membrane (NF90, MWCO 150, Polyamide TFC, Dow Filmtec), 1 kDa MWCO regenerated cellulose (RC) membrane (Ultracel, Millipore), 5 kDa MWCO regenerated cellulose (RC) membrane (Ultracel, Millipore), and a 10 kDa MWCO membrane made of a composite fluoropolymer on a polypropylene support layer (ETNA10PP, Alfa Laval, DK). Table 1 summarizes which pollutants, CDs and membranes were tested in filtration experiments.

Permeate was collected every 20–30 min and weighed (Balance, BP2215, Sartorius, DE) to determine the mass flow of permeate and thereby permeate flux. The initial feed volumes were 200 mL and filtrations were conducted till 40–70 mL feed was left (retentate). The samples were analyzed using a Dionex HPLC (Dionex Corporation, Sunnyvale, CA, USA) system, equipped with a Dionex P680 HPLC pump and a UV detector (Dionex UVD 170U). Additionally, the concentration of pollutants in feed/retentate was measured in the beginning and end of filtration experiments. A C18 column (Kinetex 5 µm EVO C18 100 Å, Phenomenex, CA) was used, and BPA was analyzed with an eluent composed of 60% Acetonitrile and 40% MilliQ water and detected at a wavelength of 230 nm. IBU was analyzed using an eluent composed of 55% Acetonitrile and 45% MilliQ water and detected at a wavelength of 220 nm, while phenol was analyzed using an eluent consisting of 70% phosphate buffer (pH = 2.55) and 30% acetonitrile and was detected at a wavelength of 270 nm. Data was analyzed using the Chromeleon software (Dionex Client 6.60 SP1 Build 1447, Dionex Corporation, Sunnyvale, CA, USA).

2.3. Binding properties between pollutants and CDs

The binding properties between HP-β-CD and β-CD polymer as host molecules and phenol and IBU as guests were studied by isothermal titration calorimetry (ITC) to determine the binding constant. A MicroCal Auto-iTC200 microcalorimeter was used for measurement and subsequently the software MicroCal PEAQ-ITC was used for data analysis. Each titration consisted of 11 injections of aqueous CD-solution (10 mM) to the cell, containing an aqueous solution of the guest molecule (1 mM). Injections were added the cell with a spacing of 150 s and injection volume was 3.7 µL. The titrations were performed at 25 °C with a stirring speed of 750 rpm. Control measurements were performed to determine potential heat of dilution. The heat flow peaks were integrated and normalized by subtracting relevant control measurements, and the software was used to determine the binding constant ($K_{1:1}$) by fitting the data to a theoretical titration curve, assuming a 1:1 binding complex.

3. Results and discussion

3.1. Binding strength of inclusion complexes

The binding constant was measured with ITC calorimetry and determined assuming 1:1 complex formation between IBU and phenol guest molecules and HP-β-CD and β-CD polymer, as shown in Table 2, along with a literature value for the complexation between BPA and HP-β-CD. It should be noted that the HP-β-CD used in the literature value has a higher degree of substitution than the HP-β-CD used in the current study, hence there are a higher number of hydroxypropyl groups substituted on the CDs (Cai et al., 2020). The highest binding strength is observed between BPA and HP-β-CD (14940 M^{-1}). The data shows that the binding strength between CDs and IBU is more than one order of magnitude higher than between CDs and phenol. In addition, the binding strength is higher between IBU and HP-β-CD (3584 M^{-1}) compared to the complex between IBU and β-CD polymers (1908 M^{-1}).

3.2. Impact of CDs on pollutant retention

Fig. 1a shows the permeate concentrations measured over time during filtration of IBU solutions without and with HP-β-CD and β-CD polymer using a 5 kDa membrane as a representative example. The results from other membranes are summarized in Table 3. It is observed that the concentration of IBU in all samples is lower than the initial feed concentration (10 mg/L) but increases over time. The graph clearly shows that IBU concentrations in permeate is lower for filtrations where CDs have been supplied. β-CD polymer shows the highest efficiency in reducing permeate concentration. The increase in permeate concentration over time is an effect of concentration of the feed solution in the filtration cell, leading to higher permeate concentrations. The volumetric concentration factor (VCF) can be calculated from Eq. (1):
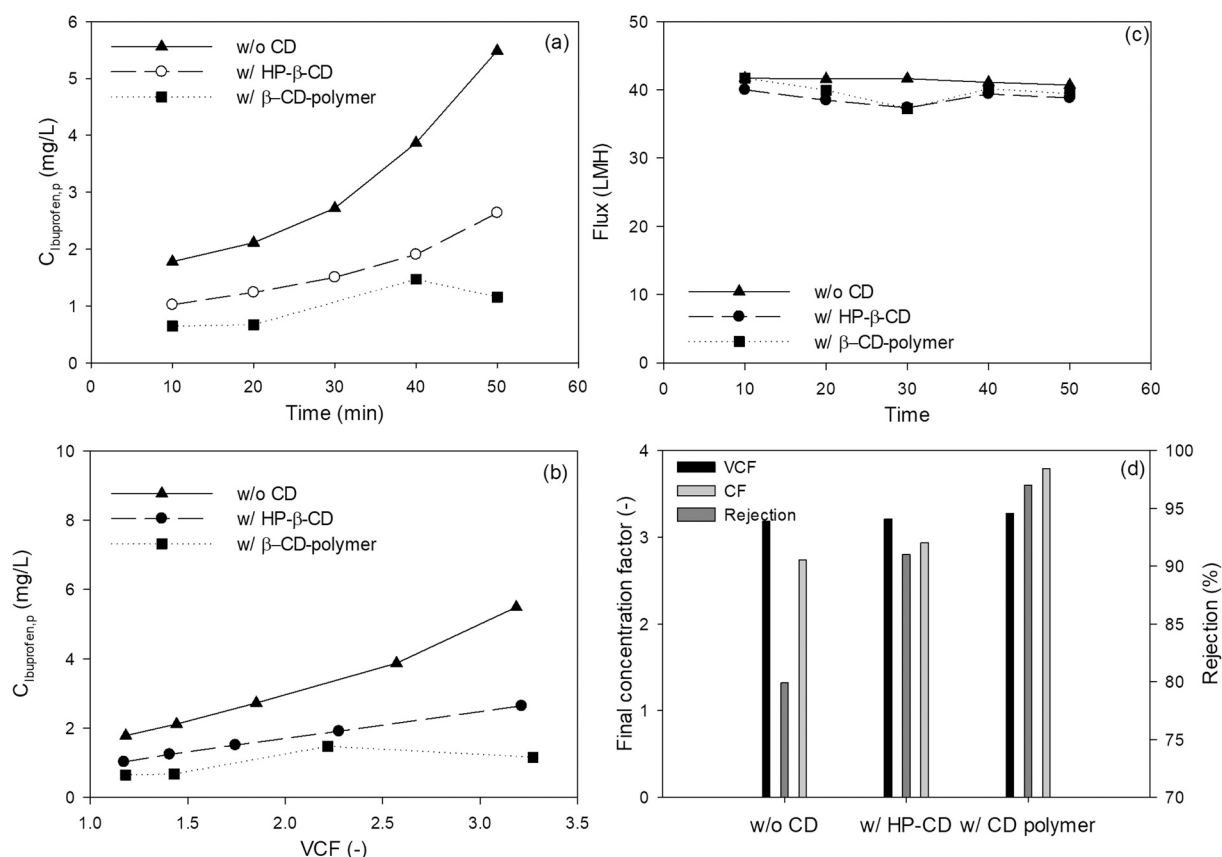
Fig. 1 – Concentration of IBU in permeate measured over time (a), different VCF (b) and flux over time (c) during filtration of 10 mg/L IBU solutions with a 5 kDa RC membrane in absence and presence of HP-β-CD and β-CD polymer and summary of VCF, CF and rejection of IBU for each filtration (d).

$$VCF = \frac{V_{f,i}}{V_{f,f}} \tag{1}$$

Where $V_{f,i}$ is the initial feed volume and $V_{f,f}$ is the final feed volume at the end of the filtration. In case of complete rejection of the pollutant, the VCF will equal the concentration factor (CF), which can be calculated as follows:

$$CF = \frac{C_{f,f}}{C_{f,i}} \tag{2}$$

Where $c_{f,f}$ is the final feed concentration while $C_{f,i}$ is the initial feed concentration. In Fig. 1b the permeate concentrations of IBU during filtrations using the 5 kDa membrane are plotted against the VCF at the different times of sampling. This confirms the tendency that higher concentration factors lead to higher permeate concentrations of IBU, but the concentrations are reduced by the addition of CDs due to the inclusion complex formation. Fig. 1c shows the development of flux (J) during filtration, which is sable around 40 L m^{-2} h^{-1} (LMH) for filtrations with and without CDs.

The rejection (R) of pollutants is calculated by comparing the initial concentrations of pollutants in permeate ($C_{p,i}$) and feed by using Eq. (3):

$$R = 1 - \frac{C_{p,i}}{C_{f,i}} \tag{3}$$

Fig. 1d shows the VCF, measured CF and rejections calculated from the 5 kDa membrane filtration data shown in Fig. 1a as to compare the effect of addition of CDs. These show that for all three filtrations, the VCF is similar (3.18–3.27). However, the measured CF is only 2.74 without CD addition and increases to 2.94 by addition of HP-β-CD and to 3.79 by addition of β-CD polymer. The calculated rejection of IBU without CDs is 79.9% and increases to 91.0% by HP-β-CD addition and 97.0% by β-CD polymer addition. Hence, there is a clear effect of CD addition on the removal efficiency of IBU by the membrane, with the high M_w polymer addition showing the highest efficiency. However, there is still transmission of IBU during filtration using the β-CD polymer, which may be an effect of low retention of free IBU.

Table 3 – Overview of rejections (R, Eq. 3) and permeate fluxes (J) for filtrations with different membranes and IBU solutions with and without HP-β-CD and β-CD polymer.

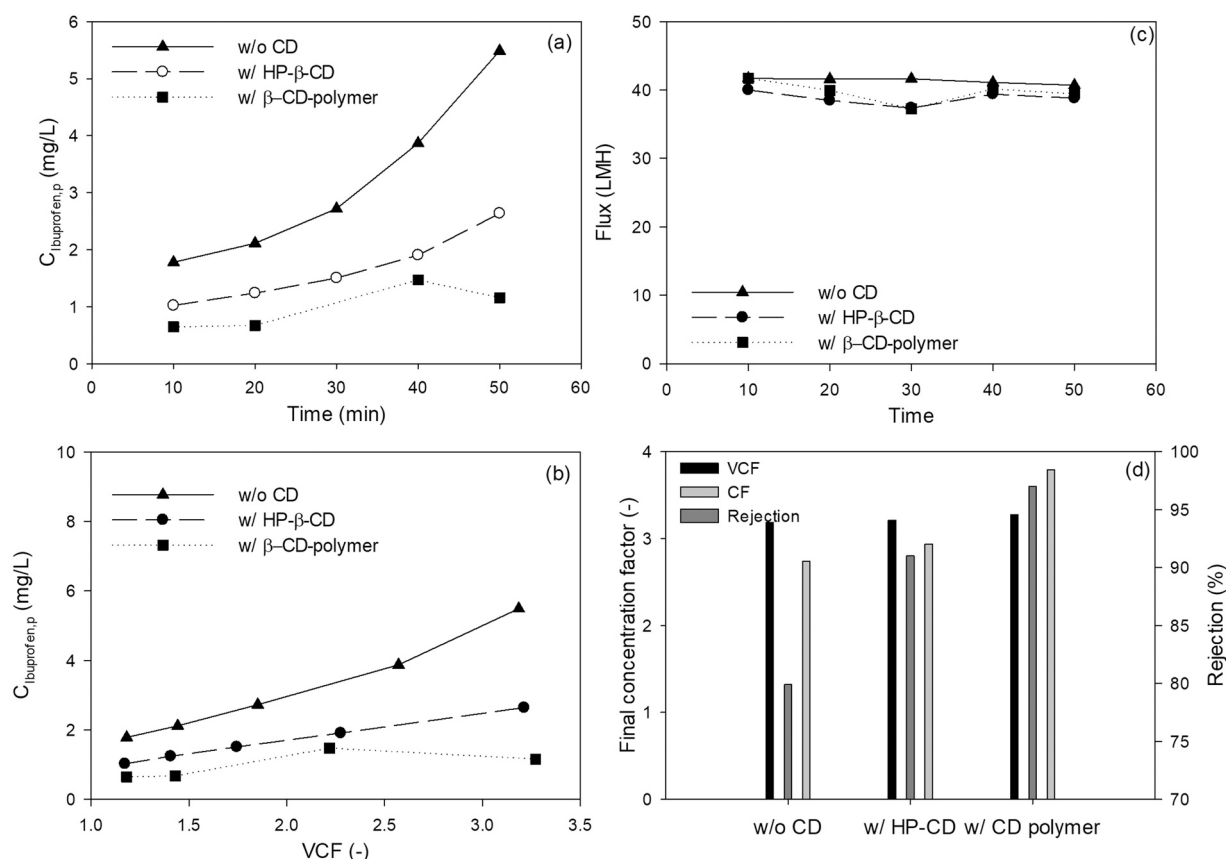| Pollutant	Membrane	Without HP-β-CD		With HP-β-CD		With β-CD-polymer	
		R	J (LMH)	R	J (LMH)	R	J (LMH)
IBU	NF90	99.5%	18	99.9%	15.9		
IBU	1 kDa	82.4%	7.6	99.3%	7.4	98.2%	6.7
IBU	5 kDa	79.9%	41.4	91.0%	37.4	97.0%	37.7
IBU	10 kDa	6.7%	250	4.8%	246		

Fig. 2 – IBU concentration evolution in permeate vs VCF during filtrations of 10 mg/L IBU solutions with and without HP-β-CD using (a) NF90 membrane, (b) 1 kDa RC membrane, (c) 5 kDa RC membrane and (d) 10 kDa ETNA membrane.

Filtrations without CD showed lower CF than VCF, which is an effect of the low retention of the pollutant. By addition of CDs, the measured CF and VCF are more similar, and for the polymer β-CD the measured CF is even higher than the VCF.

3.3. Impact of membrane on pollutant retention

In Fig. 2 the measured permeate IBU concentrations are plotted against VCF for filtrations using NF90 membrane (A), 1 kDa and 5 kDa membrane (B+C) and 10 kDa ETNA membrane (D), and the associated IBU rejections and permeate fluxes are listed in Table 3. It is evident from the graphs that the lowest IBU concentrations in permeate are reached for filtration with the NF90 membrane, while the concentration increases with higher membrane MWCO. The concentrations are also lower in permeate by presence of HP-β-CD in the feed solution, except from filtrations using the 10 kDa ETNA membrane (Fig. 2d). In the latter, the concentrations in permeate are similar with and without HP-β-CD addition and at the same level as in the feed solution before filtration (10 mg/L), which is also reflected by the low IBU rejection of 6.7% and 4.8%. This is explained by low retention of HP-β-CD (1501 Da) by the 10 kDa MWCO membrane. However, for the NF90 and the 1 kDa RC membranes, HP-β-CD has a significant effect on permeate quality. The NF90 membrane has an IBU rejection of 99.5% which increases to 99.9% by addition of the HP-β-CD to the feed (Fig. 2a). The 1 kDa RC membrane has a lower rejection of IBU (82.4%) due to the low M_w of IBU compared to the membrane MWCO of 1 kDa (Fig. 2b). It is also observed that the permeate concentration increases with VCF, starting from 1.62 mg/L at VCF 1.06–7.16 mg/L at a VCF of 3.64. For filtrations of solutions of IBU with HP-β-CD the

rejection is at a significantly higher level (99.3%) and a more constant, low concentration of IBU with VCF; 0.33 mg/L at VCF 1.06 and 0.30 mg/L at a VCF of 3.38 (Fig. 3b).

Although there is measured higher binding strength between HP-β-CD and IBU than CD-polymer and IBU (Table 2), the retention of IBU is higher for filtrations with addition of CD-polymer than HP-β-CD using 1 kDa and 5 kDa membranes. This is explained by the higher M_w of CD-polymer than HP-β-CD, leading to a higher CD retention and therefore higher IBU retention.

Another effect of varying membrane MWCO is the permeability. Table 3 shows that permeate fluxes (J) are higher for 5 kDa and 10 kDa membranes (37.4–250 L m^{-2} h^{-1} (LMH)) compared to NF90 and 1 kDa membranes (7.4–18 LMH), which places lower demand for membrane area, i.e. lower capital and operational expenses for micropollutant removal. It is also observed that the addition of CDs does not significantly reduce permeate flux. During nanofiltration, there is a buildup of osmotic pressure at higher concentration factors, hence higher water recoveries, which reduces flux and sets a limit to water recovery rate (Yacouba et al., 2021). However, removal of micropollutants using membranes with larger pore sizes will lead to less buildup of osmotic pressure, as salts are not retained by UF membranes in contrast to NF membranes. This enables a higher water recovery rate while maintaining low concentrations in permeate and results in production of a lower volume of more concentrated retentate (reject stream) to be treated more efficiently by AOPs (Janowska et al., 2021). For all filtrations of micropollutants with addition of CDs, the flux was constant over time but lower than for filtrations of solutions without CDs. It should be further studied in future long term filtration experiments
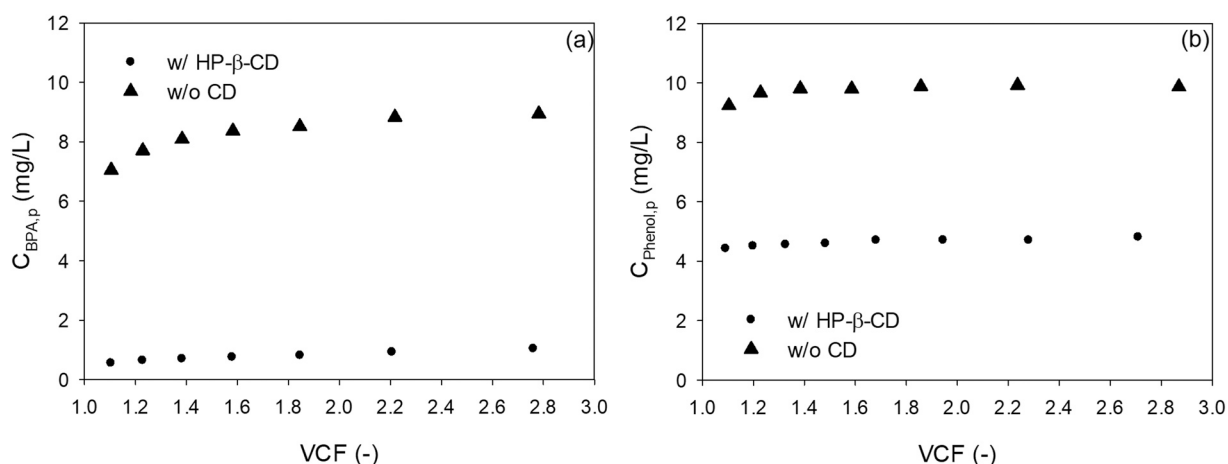
Fig. 3 – Concentration of BPA and phenol in permeate at varying VCF during filtration of 10 mg/L solutions with a 1 kDa RC membrane with and without HP-β-CD in the feed.

how permeability and fouling is affected by the addition of CDs.

3.4. Retention of different pollutants

The retention of 10 mg/L BPA and phenol with and without complexation with HP-β-CD was studied by dead-end filtrations. The 1 kDa RC membrane was selected as it in previous results show high retention of complexes ut low retention of pollutant (BPA). The permeate concentrations of pollutants vs. VCF are shown in Fig. 3a and b for BPA and phenol, respectively.

The results show similar trends as observed for IBU (Fig. 2b), i.e. increasing concentrations of pollutants in the permeate with higher VCF and lower permeate concentrations during filtration with HP-β-CD in the feed. To compare the retention of the three different pollutants with and without HP-β-CD, Table 4 summarizes the initial and final rejections (R_i and R_f) along with the measured permeate fluxes. In accordance with Fig. 3b, the rejection of phenol by the membrane is only 9.1% in the beginning of the filtration and drops to 4.0% in the end. This is explained by the low M_w of phenol (94.1 Da) compared to the membrane MWCO (1 kDa). The starting rejection of BPA is 27.9% and turns to 14% in the end of the filtration, and the rejection of IBU is 84% in the beginning and 82.4% in the end. For filtrations with HP-β-CD in the feed, there is a higher rejection of the pollutants, which initially is 98.3% for IBU, 94.5% for BPA and 56.0% for phenol. By the end of filtration, the rejection has increased to 99.3%, 96.4% and 76.4%. Hence, there is a general trend that by reducing volume and concentrating solutions of pollutants and HP-β-CD the rejection increases, which is the opposite of the declining rejection observed for filtrations without CDs. The lower rejection of phenol than IBU and BPA is in line with the lower binding strength with HP-β-CD as

observed in Table 2. The higher binding strength between BPA and HP-β-CD (14940 M^{-1}) compared to IBU and HP-β-CD (3584 M^{-1}) would suggest a higher retention by the 1 kDa membrane. However, the highest retention is observed for IBU, which may be a consequence of higher rejection due to higher hydrated radius of negatively charged IBU (from Na-IBU salt, 0.69 nm (Bešter-Rogač, 2009)) compared to uncharged BPA (0.47 nm, no salinity (Zhao et al., 2015)).

3.5. Simulation of the impact of concentration factor on pollutant rejection

The enhanced rejection of pollutants by the addition of CDs is a result of the following equilibrium to form an inclusion complex:

$$G + CD \rightleftharpoons G - CD$$
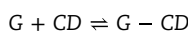
Which has the equilibrium constant expressed in Eq. (4):

$$K_{1:1} = \frac{C_{G-CD}}{C_G \cdot C_{CD}} \tag{4}$$

In which C_{G-CD} is the concentration of complexes between CD and guest molecules, C_G is the guest molecules concentration and C_{CD} is the concentration of free CDs.

By concentrating the solution by NF, the equilibrium is expected to shift by two counteracting mechanisms; First, as pollutant permeates through the membrane, the equilibrium may shift to the left, i.e. pollutant is released from the inclusion complex. However, as the pollutant and CD are concentrated, and if $C_{CD} >> C_G$, the equilibrium will shift to the right. To understand how the equilibrium is affected by NF, the equilibrium formation is studied by simulations of filtrations in MATLAB. For the simulations, a feed and bleed crossflow NF system is assumed, as depicted in Fig. 4a, and it is assumed that free CDs and CDs in complex have 100%

Table 4 – Initial and final pollutant rejections and permeate fluxes measured in dead-end filtrations using 1 kDa RC membranes in the presence and absence of HP-β-CD in the feed.

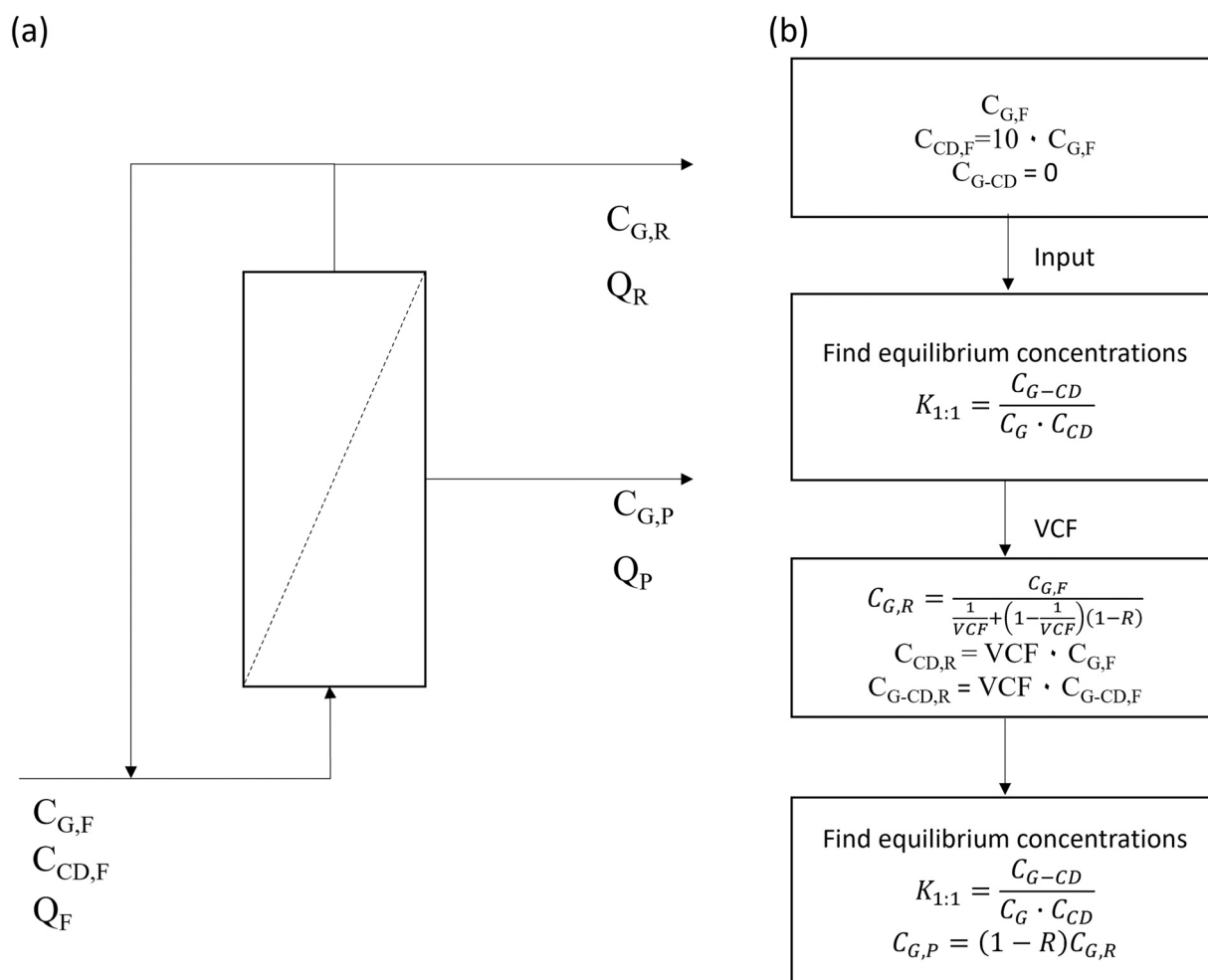| Pollutant	Membrane	Without HP-β-CD			With HP-β-CD		
		R_i (VCF=1)	R_f (VCF)	J (LMH)	R_i (VCF=1)	R_f (VCF)	J (LMH)
IBU	1 kDa RC	84.0%	82.4% (3.64)	7.6	98.3%	99.3% (3.38)	7.4
BPA	1 kDa RC	27.9%	14.0% (2.78)	12.4	94.5%	96.4% (2.76)	12.4
Phenol	1 kDa RC	9.1%	4.0% (2.87)	12.6	56.0%	76.4% (2.71)	10.7

(a)

(b)

Fig. 4 – Illustration of simulated feed and bleed NF system (a) and procedure for simulation of guest molecule complexation and retention in NF with CDs (b).

rejection by the membrane. A diagram for rejection as function of VCF is presented in Fig. 3b.

First, the chemical equilibrium, Eq. (4), is solved to find equilibrium concentrations of CD's, pollutant and CD's in complex. Second, the concentration of pollutants and CD's is expressed from the VCF. For this, a pollutant mass balance between feed, retentate and permeate can be rewritten to express retentate concentration as function of feed concentration and rejection:

$$C_{G,R} = \frac{C_{G,F}}{\frac{1}{VCF} + \left(1 - \frac{1}{VCF}\right)(1 - R)} \quad (5)$$

Whereas the concentration of pollutant in permeate is expressed by Eq. (6):

$$C_{G,P} = (1 - R)C_{G,R} \quad (6)$$

Third, the chemical equilibrium, Eq. (4), is solved again, as the concentration of compounds shifts the equilibrium. Finally, the apparent rejection is calculated by taking pollutants dissolved and in complex with CDs into account.

$$R_a = 1 - \frac{C_{G,P}}{C_{G,R} + C_{G-CD}} \quad (7)$$

$C_{G,P}$ and $C_{G,R}$ is the concentration of guest molecules in permeate and retentate, respectively.

Fig. 5 shows the variation in permeate concentrations and apparent rejection of phenol and IBU with and without

addition of HP-β-CD. Therefore, the binding constants $K_{1:1}$ = 122 M^{-1} and $K_{1:1}$ = 3584 M^{-1} are used for phenol and IBU, respectively. The rejections used in the model are the rejections without CD addition from Table 4, i.e. R = 9.1% for phenol and R = 84.0% for IBU. In the simulations, HP-β-CD is added in a molar concentration that is ten times higher than the molar feed concentration of phenol and IBU, which is $C_{G,F}$ = 1 mmol/L. The rejections are simulated for varying VCF in the range 1–10 along with permeate concentrations of guest molecules.

Comparing Fig. 5a and b confirms that the addition of HP-β-CD results in enhanced rejection of IBU and allows operation at high VCF while maintaining a high permeate quality in terms of constantly low IBU concentrations. Without addition of HP-β-CD, the rejection is low, and leads to higher permeate IBU concentrations with higher VCF. The same tendency is observed for phenol (Fig. 5c and d). In Fig. 5c it is observed that the filtration of a phenol solution with HP-β-CD results in an initial increase with VCF, which can be attributed to the higher concentrations of phenol in retentate. However, as VCF exceeds 2.1 the phenol concentration decreases with VCF. This is explained by the higher concentrations of CDs in the feed, which shifts the equilibrium of complexation to the right to form more complexes. To further explore the effect of CDs on the rejection, a NF feed and bleed filtration of 1 mmol/L phenol is simulated for varying VCF and with varying amounts of HP-β-CD (1, 2 and 10 mmol/L) in the feed.
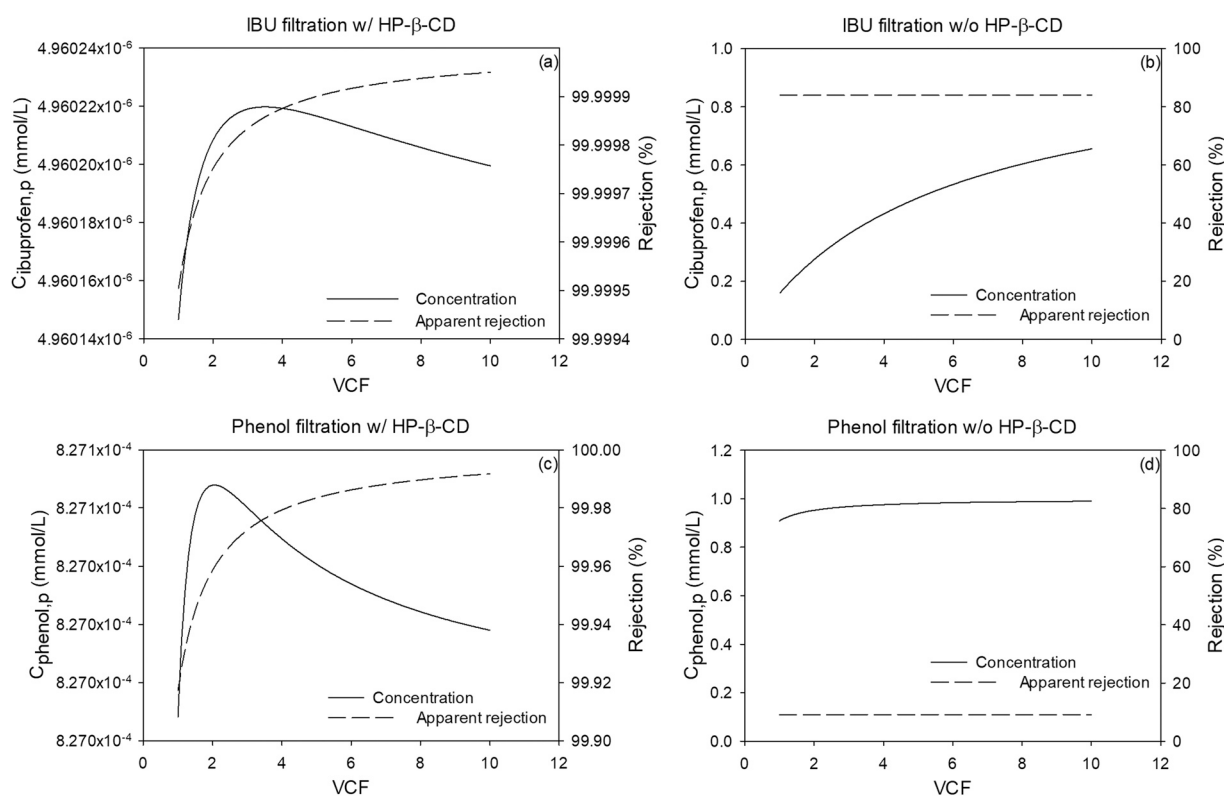
Fig. 5 – Simulated rejections and permeate concentrations of IBU (a+b) and phenol (c+d) with (a+c) and without (b+d) addition of 10 mmol/L HP-β-CD during feed and bleed filtration using a 1 kDa RC membrane. Feed concentrations of IBU and phenol were 1 mmol/L. Input data for initial rejections and $K_{1:1}$ binding constants are selected from Tables 2 and 4.

Fig. 6 shows an increasing rejection with increasing concentration of HP-β-CD and increasing VCF. The higher rejection with higher VCF observed by simulation of complexation and filtration confirms the tendencies observed from the filtration experiments, summarized in Table 4. When VCF increases, the rejection of pollutants increases due to the enhanced complexation with HP-β-CD, resulting from increasing HP-β-CD concentrations. Therefore, the addition of CDs is a promising solution to enhance rejection of micropollutants in water and wastewater treatment. Assuming a bulk cost of €0.10 /g HP-β-CD, the costs for CD dose of 1 mg/L will result in a cost of €0.10 /m³ of wastewater to be treated. According to Costa and de Pinho (Costa and de Pinho, 2006), the operational expenses for NF for
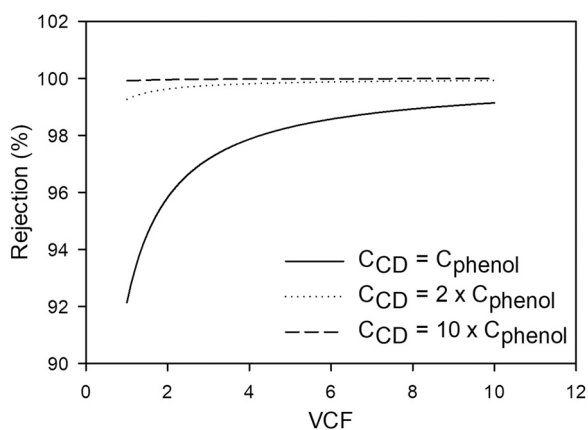
drinking water production (capacity is 100,000 m³ permeate/ d) has been estimated to €0.214/m³. Hence, the cost of addition of HP-β-CD would add to the expenses of operation of NF systems, but it will also allow for selection of higher MWCO membranes, which will result in lower membrane areas and TMP, hence lower operational costs, higher permeate quality, and finally operation at higher VCF, i.e. less retentate production.

The solution proposed in this study has potential for efficient polishing of effluent from wastewater treatment or drinking water treatment to remove micropollutants. Future studies should investigate the long term performance of the solution along with the possibility to fixate CDs on larger polymers or particles to allow for filtration with microfiltration membranes, enabling higher permeate fluxes, less membrane area and higher water recovery rates.

4. Conclusions

It is demonstrated for the first time that complexation between micropollutants and CDs as a pretreatment can significantly enhance micropollutants removal by membrane filtration. Not only does the addition of CD compounds enhance rejection of micropollutants during NF, it also enables separation of low M_w micropollutants (> 300 Da) by using UF membranes with 1–5 kDa molecular weight cutoffs. This enables removal of micropollutants at higher fluxes recovery, as a result of the higher permeability of UF membranes than NF membranes.

By supplying an excess of CDs compared to micropollutant guest molecules, a high degree of complexation is ensured at high concentration factors. Hence, the low loss of free guest molecules by permeation through the membrane

Fig. 6 – Simulated rejections of phenol with VCF at varying relationships between concentration of phenol and HP-β-CD during feed and bleed filtration using a 1 kDa RC membrane.

is counterbalanced by the shift in equilibrium by the higher concentration of host molecules during concentration. This leads to a higher intrinsic rejection as the contaminated water is concentrated. This combined with the operation using UF membranes will potentially enable significantly higher concentration factors of contaminated waters, hence lower volumes of retentates to be treated by e.g. AOPs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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