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Removal of selected pharmaceuticals in an ultrafiltration-activated biochar hybrid system

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ABSTRACT

In this study, selected target pharmaceuticals (PhACs) including ibuprofen (IBP), 17 α-ethinyl estradiol (EE2), and carbamazepine (CBM) were removed by an ultrafiltration-activated biochar hybrid system (UF-ABC). Based on characteristic analysis, ABC, a by-product of combustion of waste, is a promising alternative to commercially available powdered activated carbon (PAC) due to its enhanced aromatization and porous properties. Three different systems, including UF only and UF-ABC with/without humic acid (HA) were evaluated. The average retention rate of target PhACs within the UF-ABC system (without HA: 45.2%, and with HA: 34.4%) was much higher than that of the UF only (15.4%), suggesting that hydrophobic adsorption by ABC was the dominant mechanism. In addition, although fouling is expected in UF-ABC due to the presence of ABC, the flux decline of UF-ABC showed similar flux behavior to that of the UF only system. The UF-ABC was compared to UF-PAC with respect to retention rate and permeate flux. The average retention rate for the target PhACs was slightly higher in UF-PAC (46.6%) than in UF-ABC (41.4%) for the target PhACs. However, UF-ABC was considered to be a good alternative system because the normalized flux of UF-ABC (0.85 and 0.77) was superior to UF-PAC (0.76 and 0.70) in the absence/presence of HA, respectively. Consequently, UF-ABC was shown to be a suitable alternative to UF-PAC with respect to both retention and fouling reduction.

1. Introduction

Contaminants of emerging concern (CECs) as rising micro-pollutants in contemporary water issues have received attention [1,2]. These distributed chemicals, which result from overuse and discharge of pharmaceutically active compounds (PhACs) / personal care products (PPCPs), and endocrine-disrupting compounds (EDCs) have been detected in water sources worldwide and have adverse effects such as by-product formation, toxicity, inhibition of metabolic processes, and disruption of ecosystems [3,4]. Ibuprofen (IBP) is pain killer PhAC that is used globally as a nonsteroidal anti-inflammatory drug [5]. The synthetic hormone, 17 α-ethinyl estradiol (EE2) has become a widespread problem because it readily accumulates in sediment and is highly resistant to decomposition [6]. Carbamazepine (CBM) is the most widely prescribed pharmaceutical for epilepsy and readily bioaccumulates in the aquatic environment [7]. These micropollutants cannot be completely removed by conventional water and wastewater treatment processes, such as coagulation-sedimentation-filtration and activated sludge processes [8,9]. Therefore, effective and efficient technologies are necessary for water treatment, to facilitate the safe use of water sources.

Membrane technology has been increasingly applied to treat a variety of water sources [10]. Membrane technology is a physical process driven by pressure, which separates CECs via different mechanisms including hydrophobic adsorption [11], steric/size exclusion [12], and electrostatic interaction [13]. Ultrafiltration (UF) has numerous advantages, such as relatively low energy consumption, competitive cost, and ease of operation. However, in UF systems, membrane

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fouling is still an unresolved problem and the removal efficiency is low in comparison to high-pressure membrane technologies, such as reverse osmosis and nanofiltration [1]. To overcome these disadvantages of UF systems, hybrid system, surface modification [12], and multi-step membrane processes [14,15] have been studied. Especially, adsorption is generally applied as a pretreatment to the UF system, due to simple operation, relatively low cost, and effective elimination of organic compounds. The combination of UF with commercial powdered activated carbon (PAC) for removal of CECs has been studied [16–18].

Activated biochar (ABC), a promising alternative adsorbent, is derived from pyrolysis of black carbon waste biomass at relatively low temperatures in low oxygen conditions [19,20]. ABC effectively removes various pollutants, including nutrients, heavy metals, and various CECs, from aqueous systems due to its high surface area and porous, aromatic structure [21,22]. Jung et al. reported that seven EDCs/PhACs could be adsorbed to ABC better than to commercially available PAC under various experimental conditions [23]. Yao et al. found that 2–14% of sulfamethoxazole remained in reclaimed water transported to soil with biochar, while 60% of sulfamethoxazole was measured in leachate without biochar [24]. Studies have reported that the effect of PAC on flux is still unclear in absorbent-membrane hybrid systems [25]. Most studies of integrated UF and adsorption systems were conducted using PAC as absorbent, resulting in limited information on membrane fouling and water permeability within a combined UF with ABC hybrid system (termed a 'UF-ABC system' in our study).

Therefore, the main purpose of this study was to investigate the feasibility of a UF-ABC system by comparing the characteristics of lab-made ABC and commercially available PAC. The removal of selected PhACs in the UF-ABC system is discussed and the role of ABC in membrane flux decline is evaluated in the presence or absence of natural organic matter (NOM) for a better understanding of behavior in real aquatic environments. IBP, EE2, and CBM were selected as target compounds, since they are commonly detected in various aquatic conditions. Experiments were conducted under various pH conditions, where the physicochemical properties of those compounds (*e.g.*, charge and hydrophobicity) vary significantly.

2. Materials and methods

2.1. Preparation of ABC and characterization

A commercially available PAC was purchased from Sigma-Aldrich (Darco-KB-G; St. Louis, MO, USA), and a sample of ABC was prepared in the laboratory. A loblolly pine sample with bark (15 mm × 6 mm) was dried at 300 °C for 15 min in a bath-type tube-furnace to produce ABC. A gas of 7% oxygen and 93% nitrogen was used in the experiments, as described elsewhere [23]. The biochar was activated with 4 M NaOH for 2 h and dried overnight at 105 °C. Then the ABC was separated from the NaOH solution using a Buchner filter funnel, heated at 800 °C for 2 h under a 2 L/min nitrogen gas flow, and cooled at a rate of 10 °C/min. The dried ABC was rinsed alternately with deionized (DI) water and 0.1 M HCl to obtain pH 7 and dried again at 105 °C. Finally, the ABC was milled and passed through a 74-μm sieve.

The ABC was characterized via an elemental analysis (2400 Series II elemental analyzer; PerkinElmer, Waltham, MA, USA). In addition, the Brunauer-Emmett-Teller (BET) specific surface area (SSA) and Barrett-Joyner-Halenda (BJH) pore volume (N_2 at $P/P_0 = 0.95$) were measured using a surface analyzer (Germini VII 2390; Micromeritics, Norcross, GA, USA).

2.2. Solutions and analysis

The three PhACs (IBP, EE2, and CBM) selected for this study were purchased from Sigma-Aldrich. Detailed physicochemical properties are summarized in Table 1. These compounds have different characteristics, such as molar weight, acid dissociation constant (pK_a), and octanol-water partition coefficient (K_{OW}). The 10 mM stock solutions of IBP, EE2, and CBM were prepared in methanol to achieve a cosolvent effect. Each solution of 10 μM concentration was placed in a separate beaker and the methanol was evaporated, before dilution with ultrapure DI water. To ensure the same level of methanol evaporation, each beaker was under a fume hood at room temperature for 2 h.

The pH and conductivity were adjusted to desired values (*e.g.*, pH 3.5, 7, and 10.5; conductivity 300 μS/cm) using 1 M HCl or NaOH with 1 mM phosphate buffer solution and 0.1 M NaCl, respectively. Humic acid (HA), one of the most commonly dissolved NOM compounds, was purchased from Sigma-Aldrich. First, 1000 mg/L of HA stock solution was prepared in DI water and filtered sequentially through a 0.45 μm filter. This HA stock solution was then further diluted with DI water to 5 mg/L and dissolved organic carbon (DOC) was added in several separate experiments.

The concentrations of IBP, EE2, and CBM were analyzed using high-performance liquid chromatography with UV detection (100 Series; Agilent, Santa Clara, CA, USA). Compounds were placed in a 2 mL amber vial. A 5 μm column (Atlantis T3; Waters, Milford, MA, USA) was used at a flow rate of 1.2 mL/min. The mobile phase was a 60:40 (v/v) mixture of acetonitrile and phosphoric acid (5 mM). The concentration of HA was measured using UV–vis spectroscopy (8453; Agilent) at a wavelength of 254 nm. A ZetaPALS Analyzer (Brookhaven, USA) was used to determine the zeta potential of ABC and PAC.

2.3. Operation of the UF-ABC system

A commercial flat sheet polyamide UF membrane was purchased from GE Osmonics Inc. (Minnetonka, MN, USA). The membrane properties are described in Table S1. The pure water permeability (PWP) test and hybrid system test were conducted in a dead-end cell filtration system (HP4750; Sterlitech Co., Kent, WA, USA) with a 14.6 cm^2 active membrane area and 300 mL total feed volume. Only membranes with ≤ 10% permeability change, based on the PWP test, were used for this study. The UF membrane was washed at least three times with DI water and stored by soaking in DI water at 4 °C, away from direct light, prior to use.

A mixed compound solution was used for the UF-ABC system experiment. Each 10 μM of the initial concentration of IBP, EE2, and CBM was blended in the presence and absence of 10 mg/L of ABC and 5 mg/L of HA for 4 h at 300 rpm before the membrane experiments. In many water treatment plants, the adsorption process is generally applied at 5–50 mg/L with contact times of 1–5 h [26]. The membrane experiments were conducted with the transmembrane pressure and stirring speed set to 520 kPa (75 psi) and 300 rpm, respectively. To analyze the retention rate of selected compounds, permeate samples were obtained every 20 mL until a permeate volume of 240 mL and retentate volume of 60 mL was reached, corresponding to a volume concentration factor (VCF) of 5. The VCF (ratio of initial feed volume to concentrate volume) was calculated using Eq. (1) [27]:

$$VCF = \frac{V_F}{V_R} = 1 + \frac{V_P}{V_R} \tag{1}$$

where V_F (mL), V_P (mL), and V_R (mL) are the initial volume of feed, volume of permeate, and volume of retentate, respectively.

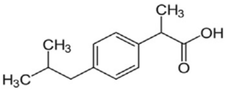
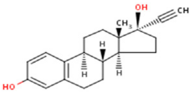
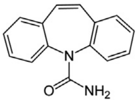
2.4. Evaluation of UF-ABC system performance

In the membrane experiments, the retention rate of selected PhACs and flux decline were investigated to evaluate the UF-ABC system. The retention rate is defined by Eq. (2):

$$Retention\,(\%) = \left(1 - \frac{C_{p,VCF}}{C_{f,0}}\right) \times 100 \tag{2}$$

where $C_{f,0}$ (mg/L) is the initial concentration of selected

Table 1
Physicochemical properties of the selected PhACs in order by p*K*a.

Compound (Formula) [ID]	Structure	MW (g/mol)	log D_{OW}[a]			Log K_{OW}	pK_a[a]	Mol. Dimension (Å)[b]	Vol[a] (Å^3)	Mol. Polarity[a]	π Energy[a]
			pH 3.5	pH 7.0	pH 10.5						
Ibuprofen ($C_{13}H_{18}O_2$) [IBP]		206.3	3.84	1.82	0.60	3.84	4.52	L: 10.98 H: 4.33 W: 5.31	211.8	23.7	15.7
17 α-ethinylestradiol ($C_{20}H_{24}O_2$) [EE2]		296.4	3.90	3.90	3.57	3.90	10.47	L: 12.28 H: 6.23 W: 3.77	291.7	33.9	18.5
Carbamazepine ($C_{15}H_{12}N_2O$) [CBM]		236.3	2.77	2.77	2.77	2.77	13.96	L: 9.43 H: 5.92 W: 7.38	210.3	27.0	29.1

[a] Chemicalize.org by ChemAxon.
[b] Molecular dimensions calculated using MacMolPlt v.7.4.

pharmaceuticals in feed, $C_{p,VCF}$ (mg/L) is the concentration in permeate at corresponding VCF. The dominant mechanism of compound removal was analyzed based on retention rate, obtained via a mass balance. For the UF membrane process, there are various removal mechanisms, including those based on size/steric exclusion, adsorption, and charge effect. However, the rate of removal of IBP, EE2, and CBM is mainly determined by both adsorption and charge effect, while size/steric exclusion plays a negligible role because the compounds are too small relative to the membrane pore. Therefore, retention of mass is equal to the sum of retention of adsorption and charge effect, as quantified by Eq. (3):

$$Retention_{mass}(\%) = Retention_{adsorption}(\%) + Retention_{charge}(\%) \tag{3}$$

An electronic balance (AV8101C; Ohaus, Parsippany, NJ, USA) was used to determine the permeate mass, and the flux decline was calculated using Eq. (4):

$$J= \frac{d_m}{\rho A_m d_t} \tag{4}$$

where *J* is the permeate flux (L/m^2/h), *m* is the mass of permeate (kg), *ρ* is the density of permeate solution at 20 °C, A_m is the active membrane area (m^2), and *t* is the sampling time (h).

3. Results and discussion

3.1. Characterization of ABC and PAC

The elemental compositions, specific surface area (SSA), and pore volume of ABC and PAC were characterized and quantified by an elemental analysis and a surface analyzer, respectively; the results are shown in Table 2. ABC has a higher oxygen content (13%) than PAC (7.7%), because ABC with pyrolysis in the presence of oxygen was partly combusted. While the carbon content of ABC (83.8%) was higher than that of PAC (79.1%), the ash content of ABC (2.7%) was lower than that of PAC (9.8%). In addition, the polarities [(O + N)/C] of PAC (0.07) were lower than those of ABC (0.12), indicating that PAC has a slightly higher hydrophobicity compared to ABC [28,29]. On the other hand, the H/C ratios of 0.03 for ABC and 0.52 for PAC indicated that ABC was carbonized to a greater extent, and had a higher degree of aromatization, compared to PAC [30,31].

The SSA and pore volume of the adsorbents were quantified by N_2 adsorption experiments (Table 2). PAC had a slightly larger specific surface and pore volume (1264 m^2/g and 0.93 cm^3/g, respectively) compared to lab-made ABC (1151 m^2/g and 0.63 cm^3/g, respectively). It is notable that, although the SSA and pore volume of ABC are lower than PAC, the ABC activation process is well controlled and comparable with that of commercial activated carbon. Aromatic structures may inhibit the development of SSA and the porous structure of ABC [19,23,32]. For superior adsorption capacity, effective SSA, pore volume, and absolute aromaticity are important. Therefore, given its high degree of aromatization and porous properties, ABC made from renewable biomass is a promising adsorbent.

3.2. Retention of selected PhACs by the UF-ABC system

The UF-ABC systems were used to evaluate the retention of selected PhACs under different pH conditions in the presence or absence of HA, as a function of the VCF (Fig. 1). VCF is a more practical value for evaluation of retention rate and flux decline than permeate volume or time, because the physical and chemical properties of the membrane, as well as the solute retention, were significantly affected by the concentration of PhACs and HA retained at the membrane surface during membrane filtration [33,34]. The average retention rates over the entire pH range were observed for UF only (24.4%, 14.8%, and 7.0%), UF-ABC without HA (41.8%, 53.0%, and 40.9%), and UF-ABC with HA (36.9%, 42.5%, and 23.9%) for IBP, EE2, and CBM, respectively. The average retention rates were thus in the order: IBP > EE2 > CBM in the UF only system. However, EE2 had a higher retention rate than IBP and CBM in the UF-ABC system.

Previous studies have shown that the retention mechanism of the UF

Table 2
Characteristics of ABC and PAC based on elemental composition, BET-N_2- surface area (SA-N_2), and cumulative pore volume.

Adsorbent	C (%)	H (%)	N (%)	O (%)	Ash (%)	H/C	Polarity index [(O + N)/C]	SSA-N_2[a] (m^2/g)	Pore volume[b] (cm^3/g)
ABC	83.8	0.2	0.3	13.0	2.7	0.03	0.12	1151	0.63
PAC[c]	79.1	3.4	≤ 0.1	7.7	9.8	0.52	0.07	1264	0.93

[a] Calculated using the Brunauer-Emmett-Teller (BET) equation for data in the range less than 0.1 of relative pressure.
[b] Calculated from the adsorbed quantity of N_2 at P/P_0 = 0.95 with t-plot mod.
[c] [29,49].

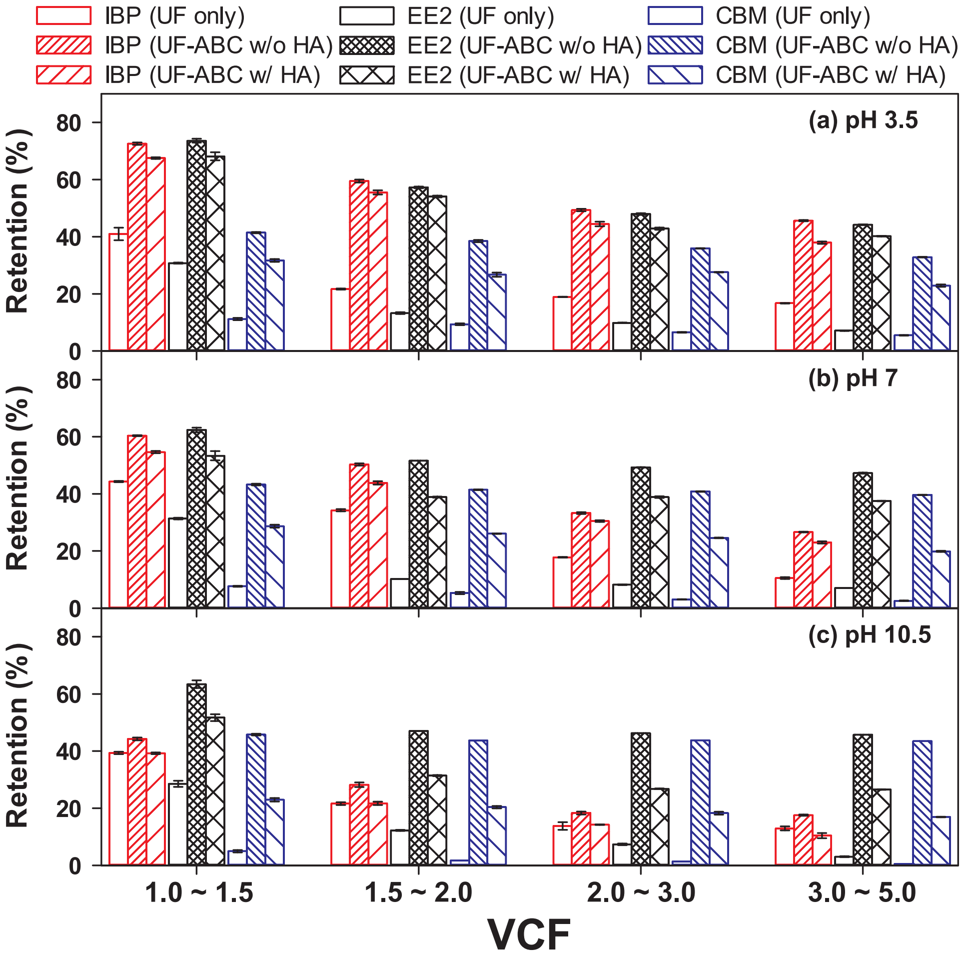


Fig. 1. Retention of IBP, EE2, and CBM by UF only, UF-ABC without (w/o) HA, and UF-ABC with (w/) HA at varying pH conditions. Operation conditions: ΔP = 520 kPa (75 psi); stirring speed = 300 rpm; HA = 5 mg/L as DOC; ABC = 10 mg/L; conductivity = 300 μS/cm; pre-contract time with ABC and HA = 4 h.

membrane system is based on interaction between the membrane and organic compounds, and on size/steric exclusion [1,35]. Even though selected compounds are mainly found in neutral ionic forms under acidic conditions, increasing the pH converts ionic forms from neutral to negative species depending on the p*Ka* value [23]. This change of ionic form leads to increasing electrostatic repulsion between the membrane and compounds. Regarding the molecular weight of selected compounds (206–294 g/mol), size/static exclusion is a negligible mechanism because the used membrane pore size (1.03 nm) and nominal molecular weight cutoff (MWCO = 3000 Da) are much larger than the compound molecules [36–39]. For the UF-ABC system, the following represent additional possible retention mechanisms for PhACs: π-π electron donor-acceptor (EDA), electrostatic interactions, and hydrophobic adsorption between ABC and selected compounds [35]. Among these retention mechanisms, the π-π EDA interactions between ABC and selected PhACs were not considered in this study. Although π-π EDA interaction between ABC and compounds can be highly affected by the π energy level of individual compounds [40], the retention rate in this study did not suggest a strong relationship between adsorbents and adsorbates. It has been reported that hydrophobic adsorption by absorbents is primary mechanism of UF-adsorbent systems [17,35]. Furthermore, our findings showed that the sharp improvement in the retention rate of UF-ABC compared to UF only can explain the effect of adsorption on ABC (Fig. 1). Although IBP has a lower octanol-water distribution coefficient (log D_{OW} = 1.82 at pH 7, which represents hydrophobicity), above pH 7 the average retention rate of IBP is similar to or slightly higher than that of CBM. These results suggest that retention in UF-ABC systems is affected by both charge effect (*i.e.,* electrostatic repulsion) and hydrophobic adsorption among compounds, ABC, and the membrane affect retention in UF-ABC systems.

3.3. Retention mechanism of the UF-ABC system

In the UF only and UF-ABC systems, the retention behavior described above is affected by the coupled influence of the ionic speciation and hydrophobicity of compounds, depending on the solution pH, compound p*Ka* value, and log D_{OW}. Fig. 2 describes in more detail the retention-based adsorption and charge effect and Fig. S1 shows the average retention rate of target compounds at various pH conditions as log D_{OW} was changed. Despite the significant effect of solution pH on the speciation and hydrophobicity of chemicals, hydrophobic adsorption is the dominant mechanism over the entire pH range in both systems, with the exception of IBP above pH 7. The retention of IBP by charge effect increased with increasing solution pH, because the PhACs chemicals were deprived of their proton at pH values above each p*Ka* value, resulting in negative charge. This mechanism indicates that electrostatic repulsion between each compound and the membrane, as well as ABC, improved when the pH value was greater than the p*Ka* value, particularly for IBP (p*Ka* = 4.52) which has a relatively lower p*Ka* value compared to EE2 (10.47) and CBM (13.96). However, the ionized IBP is barely adsorbed on aromatic adsorbents [23], resulting in sharply decreasing hydrophobicity (log D_{OW} = 3.84 at pH 3.5, log D_{OW} = 1.82 at pH 7, log D_{OW} = 0.60 at pH 10.5). Additionally, among the three PhACs, IBP is most affected by solution pH due to great variation in ionic species and hydrophobicity. For these reasons, the total retention rate of IBP was decreased by decreasing hydrophobic

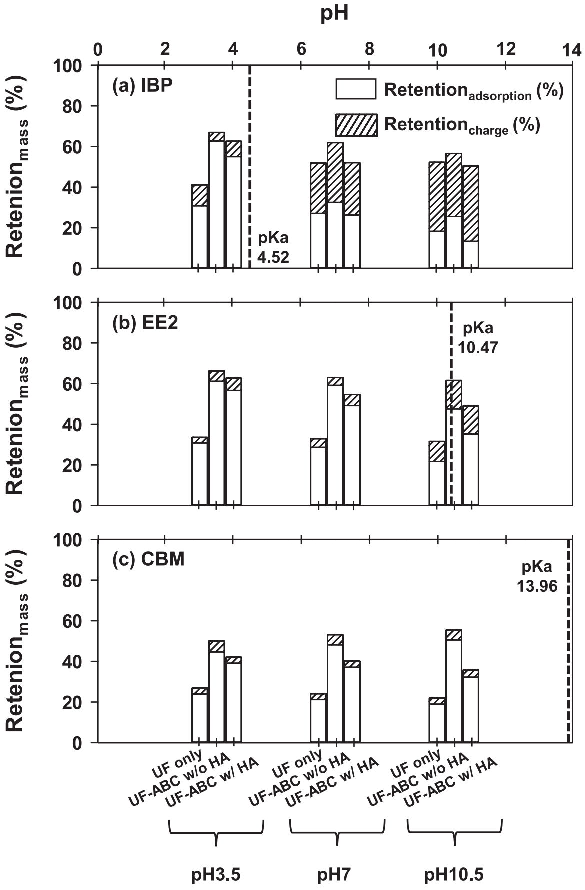


Fig. 2. Comparison of retention based on mass for UF only, UF-ABC without HA, and UF-ABC with HA. Operation conditions: ΔP = 520 kPa (75 psi); stirring speed = 300 rpm; VCF = 5; HA = 5 mg/L as DOC; ABC = 10 mg/L; conductivity = 300 μS/cm; pre-contract time with ABC and HA = 4 h. Vertical dashed lines indicate p*K*a values of each target adsorbate.

adsorption from pH 3.5 to 10.5. These results suggest that although charge effect is an important mechanism, hydrophobic adsorption was more effective in terms of retention of IBP.

The retention rates of EE2 and CBM for the three different systems was relatively constant. The ionic form of EE2 changed from neutral to negative only at pH 10.5. The dissociated EE2 improved charge effect but was not easily adsorbed on ABC or the membrane, as described previously. This phenomenon can be explained by the log D_{OW} values of EE2 of 3.90, 3.90, and 3.57 at pH 3.5, 7, and 10.5, respectively. The altered hydrophobicity of EE2 indicates that, although electrostatic repulsion is slightly increased at pH 10.5, EE2 has a constant retention rate over a wide range of pH conditions due to still relatively high hydrophobic adsorption. The CBM was non-ionizable over the pH range of the experiment, and was mostly controlled by adsorption, resulting in less variability in retention rate. In addition, the results show that adsorption on ABC can play a critical role with respect to the retention rate.

Fig. S2 and Fig. 3 present the removal rate by adsorption for seven adsorbent cases in UF-ABC with HA. As a general observation, the adsorption of each compound increased with contact time (Fig. S2), while the adsorption rate was found to vary depending on the properties of each adsorbent (Fig. 3). Removal by adsorption of the selected PhACs increased significantly in the presence of both ABC and membrane, because chemicals can be adsorbed on both materials. This explains why the retention rate of IBP was higher than that of EE2 and CBM in the UF only process: IBP, which is the most negatively charged among the selected PhACs, is retained more on the feed side. In the UF-ABC system, hydrophobic adsorption on the ABC is the dominant mechanism and the rate of chemical removal positively correlates with the hydrophobicity of each of the selected PhACs. The adsorption of organic compounds could be improved with HA due to HA-PhACs partitioning [9]. However, competition for adsorption sites between HA and the chemicals was greater relative to the adsorption of chemicals on the HA.

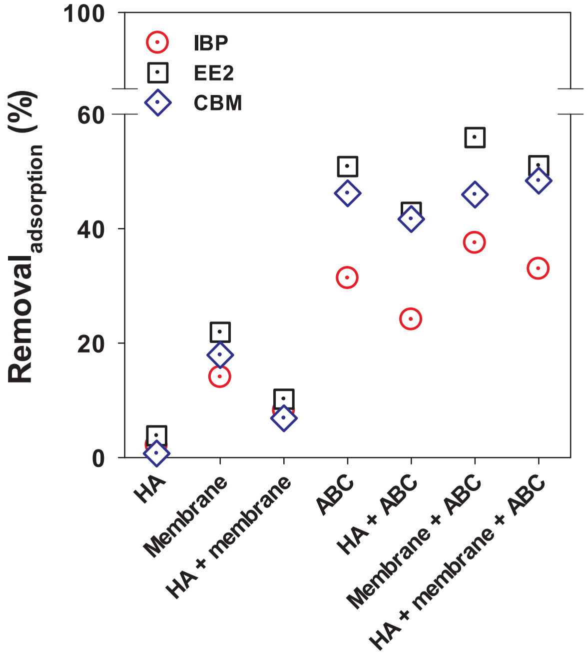


Fig. 3. Adsorption of IBP, EE2, and CBM on each adsorbent with a contact time of 3 h. Operation conditions: C_0 = 10 μM; HA = 5 mg/L as DOC; membrane = 14.6 cm^2; ABC = 10 mg/L; pH = 7 at 20 °C; conductivity = 300 μS/cm; stirring speed = 300 rpm.

3.4. Flux decline in the UF-ABC system

Based on the retention rate and mechanism for selected PhACs, the UF-ABC system is a potential replacement for the UF only system. Therefore, permeate flux was analyzed for the UF only and UF-ABC systems in the presence/absence of HA, to evaluate the hybrid system. Normalized flux declining trends are shown in Fig. 4, at three pH conditions as a function of the VCF. The normalized flux was defined as the current permeate flux divided by the flux of the virgin membrane under comparable conditions. Because flux is similar for the three compounds, the average flux at each condition is represented by a single point with a standard deviation. The normalized flux of UF only and UF-ABC system without HA gradually decreased with increasing VCF. These systems show similar flux behavior regardless of pH conditions, achieving a flux of approximately 0.85. This result indicates that, although ABC is expected to cause serious fouling compared with UF only system, ABC does not strongly affect the permeate flux decline in the absence of HA when compared with the UF only system. As shown in Fig. 3, the membrane can adsorb selected PhACs. This deposition of certain compounds on membrane surface or pore may cause a flux decline by reducing the membrane pore size [16]. The ABC can deposit on the membrane surface, and can simultaneously alleviate membrane fouling by adsorbing compounds [41]. Therefore, the flux change of the UF only and UF-ABC system without HA is almost the same. On the other hand, severe flux decline was observed in the case of UF-ABC with HA. The flux decreased rapidly as the pH decreased, decreasing to 0.75, 0.77, and 0.79 for pH values of 3.5, 7, and 10.5, respectively. This serious flux decline is due to pore plugging on the membrane surface or pore (pore size = 1.03 nm), in turn due to the HA,

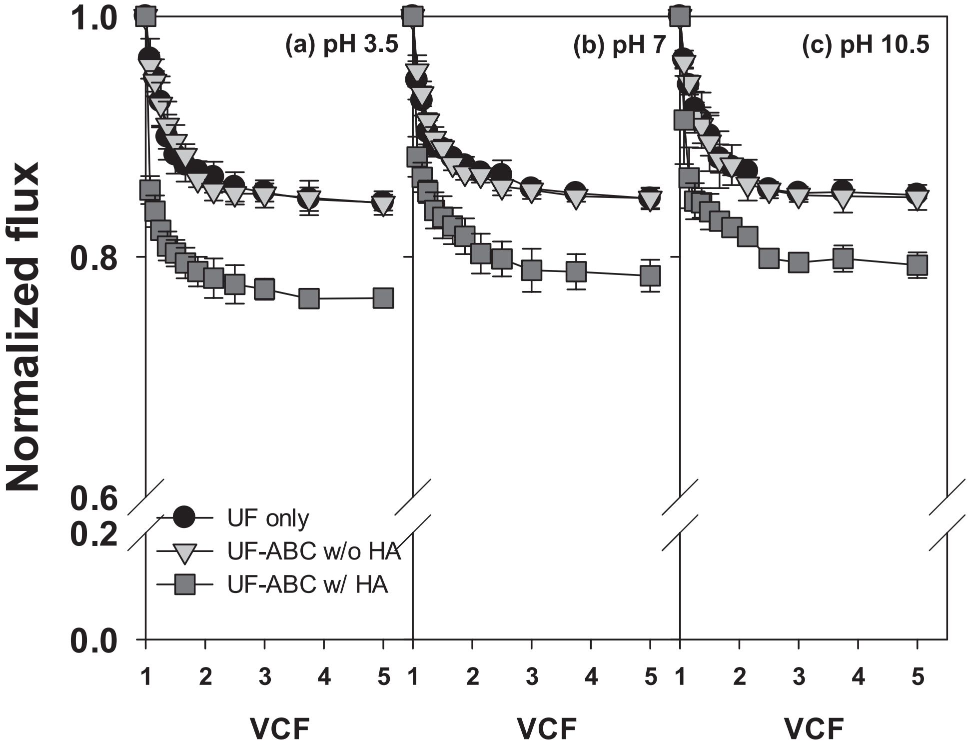


Fig. 4. Normalized flux decline for UF only, UF-ABC without HA, and UF-ABC with HA at varying pH conditions. Operation conditions: ΔP = 520 kPa (75 psi); stirring speed = 300 rpm; HA = 5 mg/L as DOC; ABC = 10 mg/L; conductivity = 300 μS/cm; pre-contract time with ABC and HA = 4 h.

which has average molecular weight in the range of 170–22,600 Da. A previous study reported that adhesion between a membrane and HA increased with decreasing pH, due to decreasing zeta potential and increasing particle size [42]. Also, Table S2 shows that the average retention rate of HA is 76.7%, 80.3%, and 83.1% at pH 3.5, 7, and 10.5, respectively. It can be inferred that more HA is present as a foulant on the membrane surface and interior membrane pores at lower pH values. Therefore, severe flux decline occurs in the UF-ABC system with HA due to hydrophobic interactions between membrane and HA under acidic conditions where membrane becomes relatively less negatively charged and HA is relatively undissociated [43].

3.5. Comparison of the UF-ABC and UF-PAC systems: retention and flux decline

Recently, combined PAC membrane systems (UF-PAC) have mostly been applied to improve the capability of membrane systems to effectively remove micropollutants [44–46]. Thus, to evaluate the capability of UF-ABC systems, UF-ABC was compared with UF-PAC in terms of retention rate and flux behavior at pH 7. Fig. 5 presents the retention rate for each of the selected PhACs in both the UF-ABC and UF-PAC systems. The results indicated that UF-PAC marginally improved retention by 4.2–7% in the absence of HA, and by 5.5–9% in the presence of HA, compared to UF-ABC. This can be explained by the elemental composition, structural characteristics, and surface properties of ABC and PAC (Table 1). First, although the stronger aromaticity of ABC improved adsorption [23,47], the lower surface area and pore volume of ABC restricted the adsorption capacity [47,48]. Furthermore, previous studies have suggested that the polarity index (O/N + O/C) positively correlates with adsorption capacity [23] and hydrophobicity [28,29], implying that a lower PAC polarity index encourages higher adsorption affinity.

The normalized permeate flux of the UF-ABC system was different to that of the UF-PAC system, as shown in Fig. 6. The results showed that the normalized flux of UF-PAC without HA was 0.76 and that of the UF-PAC with HA decreased rapidly at the beginning of the experiment, to reach about 0.70. This phenomenon is a result of fouling generated by the PhACs, PAC, and/or HA, which block the membrane surface and pores, resulting in decreased flux, as previously described in Section 3.3. Although PAC can remove PhACs by adsorbing (Fig. 5), it can be more readily deposited by interacting with the membrane due to the relatively high adsorption capacity of PAC. This resulted in a significant decline in flux in the UF-PAC. Furthermore, Fig. S3 shows that the zeta

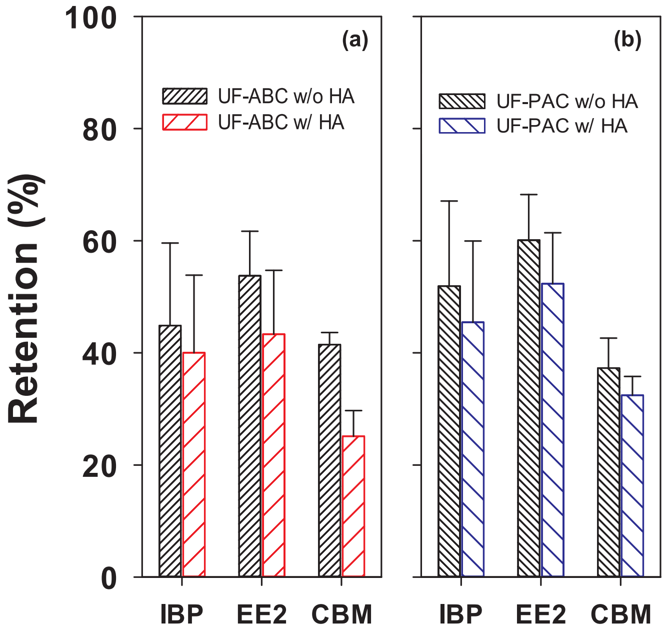


Fig. 5. IBP, EE2, and CBM retention by (a) UF-ABC and (b) UF-PAC. Operation conditions: ΔP = 520 kPa (75 psi); stirring speed = 300 rpm; pH = 7; conductivity = 300 μS/cm; HA = 5 mg/L as DOC; ABC = 10 mg/L; PAC = 10 mg/L; pre-contact time with ABC and PAC = 4 h.

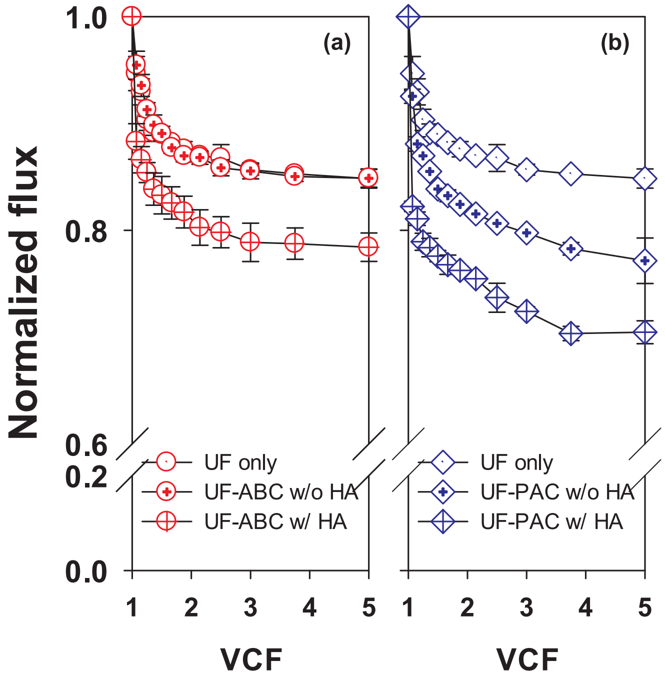


Fig. 6. Comparison of normalized flux decline: (a) UF only, UF-ABC without HA, and UF-ABC with HA, and (b) UF only, UF-PAC without HA, and UF-PAC with HA. Operation conditions: $\Delta P = 520$ kPa (75 psi); stirring speed = 300 rpm; pH = 7; conductivity = 300 µS/cm; HA = 5 mg/L as DOC; ABC = 10 mg/L; PAC = 10 mg/L; pre-contact time with ABC and PAC = 4 h.

potential values of PAC and ABC were −7.3 and −10.3 mV at pH 7, respectively. As a result, repulsion between PAC and the membrane is slightly weaker compared with ABC [42]. Although, the retention rate of UF-PAC is slightly better than that of UF-ABC due to strong hydrophobicity, surface area, and pore volume, UF-ABC was superior to UF-PAC in terms of flux decline.

4. Conclusions

In this study, an ABC generated from incomplete combustion of waste biomass, combined with UF membrane system (UF-ABC), was used to treat selected PhACs, and compared to UF-PAC. Although the ABC had a lower surface area than PAC, ABC has better aromatization. The average retention rate arranged in the following order: IBP > EE2 > CBM for the UF system alone, and EE2 > IBP > CBM for the UF-ABC system. These results were influenced by the properties (p*Ka* value and hydrophobicity) of each compound depending on the pH. However, the dominant mechanism of retention in the UF-ABC system is hydrophobic adsorption between the compounds and ABC. The UF-ABC system without HA had no serious fouling, compared to the UF system alone. However, the UF-ABC with HA demonstrated a relatively serious flux decline, because HA blocked the surface and pores of the membrane. Furthermore, although the retention rate of UF-PAC is slightly higher than UF-ABC, the UF-ABC was superior to UF-PAC in terms of flux decline. Consequently, UF-ABC may serve as a suitable alternative to UF-PAC in terms of both retention capacity and fouling reduction.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2018.10.036.

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