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Use Of Biochar-Ultrafiltration Membrane Processes For Removal Of Humic Acid

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USE OF BIOCHAR-ULTRAFILTRATION MEMBRANE PROCESSES FOR REMOVAL OF
HUMIC ACID

by

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Bachelor of Engineering
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DEDICATION

In the loving memory of my grandfather Hari Shankar Sinha. You have and will always continue to inspire me. And to my parents Vinod Kumar and Padma Rani without whose love, support and relentless efforts I would not be here.

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This work would not have been complete without the love and support of my parents Vinod Kumar and Padma Rani. Thank you ma and papa for everything that you do for me and for always being my pillars of strength. I would also like to thank my family and friends back home who regardless of the distance were always there for me and my friends here in the United States for helping me feel at home in a new country.

ABSTRACT

The performance of an ultrafiltration (UF)-biochar process was evaluated in comparison with a UF membrane process for the removal of humic acid (HA). Bench-scale UF experiments were conducted to study the rejection and flux trends under various hydrodynamic, pH, conductivity, and pressure conditions. The resistance-in-series model was used to evaluate the processes and it showed that unlike stirred conditions, where low fouling resistance was observed, comparable trends were obtained for UF-biochar and UF alone for unstirred conditions. Thus, the processes were further evaluated under unstirred conditions. Additionally, total fouling resistance was decreased in the presence of biochar, indicating that HA adsorption by biochar could significantly diminish adsorption fouling on the UF membrane and thus improve the efficiency of the UF-biochar process. The rejection trends of UF-biochar and UF alone were similar in most cases, whereas UF-biochar showed a noticeable increase in flux due to reduced membrane fouling. Three-cycle filtration tests further demonstrated that UF-biochar showed better membrane recovery and antifouling capability and thus may potentially prove be a viable treatment option for the removal of HA from water.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Natural organic matter (NOM) is known to contribute to unpleasant odor and taste in water. NOM is also a widely known precursor to potentially carcinogenic disinfection byproducts [1] and a significant contributor to membrane fouling [2]. One of the major hydrophobic components of dissolved NOM is humic acid (HA), consisting of anionic macromolecules having a wide range of molecular weights [3]. It is often accountable for severe membrane fouling due to extensive pore adsorption, making the use of membrane filtration in water treatment more challenging [4].

NOM removal from water using conventional ultrafiltration (UF) membranes has been demonstrated to be largely ineffective due to membrane fouling, restricting its widespread application as a result of increases in hydraulic resistance and operational and maintenance costs, and deterioration in productivity due to the frequency of membrane regeneration problems [5]. UF membranes alone function poorly in removing color, NOM, and synthetic organic chemicals [6]. To overcome some of these shortcomings, UF membranes have been coupled with adsorbents to develop integrated processes that meet treatment requirements and improve process efficiencies. Coupling of UF membranes with powdered activated carbons (PACs) is one of the most widely studied integrated processes [7-10], which can effectively counter irregular and unpredictable increases in odor and taste compounds. It can also enhance the productivity of the

membrane by reducing the foulant load toward the applied membrane [10]. However, if the PAC dose, membrane characteristics, and operating conditions are not monitored effectively, there can be a more severe flux decline with a PAC-UF membrane process than a UF process alone [8].

To improve the efficiency of integrated processes, newer adsorbents, such as biochar (e.g., a byproduct of bio-oil production), have been studied [11-13]. The properties of biochar are dependent on the manufacturing process and vary with the pyrolysis conditions and the type of biomass used. Short-term pyrolytic conditions with low thermal treatment (< 500°C) are known to produce an enriched, carbon-based porous biochar with properties suitable for use as an adsorbent [13]. Such biochar has favorable properties for adsorbing metal cations, such as a large surface area with a high negative charge and charge density. In addition, its hydrophobic characteristics provide affinity to adsorb hydrophobic organic compounds, such as 17α-ethinyl estradiol, diclofenac, ibuprofen [14], and NOM [15]. Biochar also exhibits superior adsorption performance to activated carbon in terms of organic removal, making it a potentially cost-effective adsorbent [11].

However, the effects of the adsorbent on membrane fouling need to be analyzed for any adsorbent used in an integrated process. The effects are a function of the physiochemical properties of the adsorbent (e.g., size, charge, and hydrophobicity), solution water chemistry (e.g., pH and conductivity), and membrane characteristics (e.g., hydrophobicity, charge, and size) [7, 9, 16, 17]. Based on these properties, the adsorbent can remove HA from the solution, which would otherwise adsorb onto the membrane pores and cause fouling, or the adsorbent may itself act as a foulant, blocking membrane pores and preventing the efficient working of the integrated process. Extensive studies have been

2

conducted on the effects of PAC on membrane fouling in an integrated process [6, 8, 10], whereas biochar, being relatively new in the field of water treatment, has been studied less in comparison.

A few studies have been reported previously on the adsorption mechanisms of NOM with biochar [13, 15, 18]. Hydrophobic HA forms π bonds with biochar and occupies the π-rich sites on the surface, acting as a π acceptor, while biochar acts as an π donor [13]. This leads to a higher adsorption affinity for HA on biochar when compared with other commercially available adsorbents, like PAC. Additionally, the presence of diverse functional groups on HA surface also promotes multi-layer adsorption with biochar due to increased adsorption via hydrogen bonding and polar interactions.

The objective of this study was to investigate the potential mechanisms for HA removal in an integrated process with a UF membrane in the presence of biochar prepared in the laboratory as an adsorbent. The effect of biochar on membrane fouling was also studied. To achieve this, flux decline and HA rejection in biochar-UF processes were investigated as a function of different solution and operating conditions, including pH, conductivity, pressure, and biochar concentration.

CHAPTER 2

MATERIALS AND METHODS

2.1. HA feed solution

HA (Sigma-Aldrich Co., St. Louis, MO, USA) was used as a representative NOM, because it is one of the most hydrophobic components of NOM, thus making its treatment more challenging. HA, with a molecular weight distribution between 180 and 22,600 Daltons, is a mixture of complex polyelectrolytes, formed chemically with hydroxylic and carboxylic functional groups [17]. To prepare the HA stock solution, powdered HA was dissolved in ultrapure deionized (DI) water and filtered consecutively through GF/F (0.7 μm) glass microfiber filters (Whatman Inc., Piscataway, NJ, USA) and Durapore (0.45 μm) membrane filters (Millipore Inc., Billerica, MA, USA) to remove any impurities and particulate matter. This HA stock solution was further diluted with DI water to obtain a concentration of 5 mg/L as dissolved organic carbon (DOC), which was used as the feed solution for rejection and flux decline experiments. The conductivity of the solution was adjusted using NaCl to maintain a final background conductivity of 300 and 11,000 μS/cm. The pH was adjusted to 4, 7, and 10 by the addition of 0.1 M HCl or 0.1 M NaOH, and was buffered with 1 mM phosphate buffer solution.

2.2 Characteristics of biochar

The biochar used in this study was produced under controlled laboratory conditions using the following process. Detailed production procedures were described in our previous report [14]. Briefly, torrefied loblolly pine chips (15×6 mm) containing bark were treated thermally at 300°C for 15 min in a laboratory-scale batch-tube furnace (OTF-1200X; MTI Corp., Richmond, CA, USA). The particular biochar used in this study was produced under a 7% oxygen + 93% nitrogen atmosphere. Next, 3 g of this pyrolyzed biochar was activated with 40 mL of 4 M NaOH for 2 h and dried overnight at 105°C. This was then heated for 2 h at 800°C under a nitrogen gas flow (2 L/min) and subsequently cooled at a rate of 10°C/min following separation from the solution using a Buchner filter funnel. The characteristics of the biochar thus produced are described in Table 1.

2.3. Biochar-UF experiments

A commercially available flat sheet polyethersulfone (PES) UF membrane (Sterlitech Corp., Kent, WA, USA), having a measured molecular weight cut-off of approximately 5 kDa, was used. The membranes were first cut to desired sizes and then washed thoroughly with DI water at least five times and preserved by soaking in DI water. To prevent microbial growth, the membranes were then stored away from direct light at 4°C. A VCA Optima process (Optima XE; AST Products, Inc., Billerica, MA, USA) was used to measure the contract angle of the UF membrane. Contact angle is a measure of the hydrophilicity of the membrane. The water droplet size of 3–5 μL, the optimal volume for producing reproducible contact angle measurements with a nominal error of ±2.3°, was

dropped cautiously onto the UF membrane. The characteristics of the membrane are described in Table 2.

Flux decline and HA rejection tests were used to evaluate performance of the biochar-UF membrane process. For all filtration tests, a dead-end stirred filtration process (Sterlitech Corp., Kent, WA, USA) was used, having a volume of 300 mL and an effective area of 14.2 cm^2. The membrane filtration set-up was coupled with a biochar reactor. An initial concentration of 5 mg/L of HA was mixed with biochar (20 mg/L) for a contact time of 2 h to simulate realistic water treatment plants conditions, where adsorbent doses of 5–50 mg/L are used over a contact period of 1–2 h [3]. The majority of UF experiments were conducted under no-stirring conditions; transmembrane pressure (TMP) was kept constant at different levels (173, 345, and 690 kPa). Also, 210 mL of permeate and 90 mL of retentate was collected for each UF experiment. The flux decline was monitored for water recovery to show fouling-related flux decline in the membrane. The concentration of HA was determined by UV-vis adsorption spectroscopy (8453 UV-vis spectrophotometer, Agilent Technologies, Santa Clara, CA, USA) at a wavelength of 254 nm, because HA solution has a characteristic adsorption peak at this wavelength. The HA rejection by the membrane was then calculated using Eq. 1:

$$R\ (feed), \% = \frac{C_F - C_P}{C_F} \times 100\% \tag{1}$$

where R is the solute rejection (removal efficiency), C_F is the HA feed concentration, and C_P is the HA permeate concentration. The permeate flux was evaluated in terms of volume concentration factor (VCF) using Eq. 2:

$$VCF = \frac{V_F}{V_R} = 1 + \frac{V_P}{V_R} \tag{2}$$

where V_F, V_R, and V_P are the volumes of feed, retentate, and permeate, respectively. The concentration of the permeate was measured every 10 mL until a VCF of 3.5 was reached.

The filtration tests were repeated three times for the UF membrane coupled with a biochar reactor and for the UF membrane with no biochar reactor. After each cycle, the membrane was rinsed thoroughly with DI water and the process was then run with a feed solution of 5 mg/L HA for the next cycle. Permeate flux and HA rejection were measured for all three cycles to investigate membrane fouling behavior and recovery capability.

2.4. Resistance-in-series model

Darcy's law can be used to describe the permeate flux (J_v) for flow through UF membranes, as in Eq. 3.

$$J_v = \frac{\Delta P}{\eta \, R_m} \tag{3}$$

where J_v is the volumetric water flux through the porous membrane (L/m^2/h), ΔP is the pressure drop across the membrane (kPa), η is the dynamic viscosity of the fluid (kg/m/s), and R_m is the hydrodynamic resistance of the membrane (1/m). During membrane filtration, many factors contribute to differing extents to the total resistance (R_t) to flow. Thus, the total resistance to flow includes (i) resistance as a result of adsorption and pore-blocking, (ii) cake resistance from the formation of a gel or porous cake through accumulation of solute on the membrane surface, and (iii) highly concentrated layer resistance toward mass transfer (i.e., concentration polarization) near the membrane surface. These resistances depend on the source water qualities in addition to the membrane operating conditions and module. In most UF applications encountered in water and wastewater treatment, concentration polarization does not appear to add any further effect to increase the

resistance after a cake layer forms near the membrane surface [19]. This indicates that concentration polarization resistance becomes a negligible resistance factor in J_v. Thus, the typical form of the resistance-in-series model for quantification of the filtration characteristics through a UF membrane containing a cake layer can be expressed with Eq. 4 [20].

$$J_v = \frac{\Delta P}{\eta \, (R_m + R_c + R_a)} \tag{4}$$

where R_c is the cake layer resistance (l/m) and R_a is the adsorptive fouling resistance (l/m).

Table 2.1. Elemental composition, aromatic ratio, ash content, aromaticity, BET-N_2 surface area (SA-N_2), and cumulative pore volume of biochar used in this study.

Samples	C %	H %	N %	O %	H/C	Polarity index		Ash %	Aromaticity[a]	SA-N_2[b] (m^2/g)	Pore volume[c] (cm^3/g)	
						N/C	O/C				micropore	macropore
Biochar	83.8	0.24	0.30	13.0	0.034	0.003	0.116	2.7	74.1	1151	0.313	0.318

[a] Aromaticity = 100 × aromatic C (108–165 ppm)/[aromatic C (108–165 ppm) + aliphatic C (0–108 ppm)].

[b] Calculated using the Brunauer–Emmett–Teller (BET) equation for data in the range less than 0.1 of relative pressure.

[c] Calculated from the adsorbed quantity of N_2 at $P/P_0 = 0.95$ with t-plot mod.

Table 2.2. Specifications and properties of membranes.

Manufacturer	Synder filtration
Membrane type	UF flat sheet
Material	Polyethersulfone
pH range	1-11
Pure water permeability* (L/m^{2}h-bar)	19.1
MWCO* (Da)	Approximately 5,000
Contact angle* (°)	69.6 ± 0.9

*Measured in our laboratory.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Influence of biochar and hydrodynamic conditions on flux decline and HA rejection

The biochar-UF process and UF alone (with no biochar) were compared in terms of flux decline trends and HA removal efficiencies. In Fig. 1a and b, normalized flux is shown as a function of VCF at a constant pH 7, conductivity of 300 μS/cm, and a pressure of 345 kPa. The normalized flux (current permeate flux divided by the corresponding initial flux) is used to provide dimensionless values of flux for a more reasonable comparison between different conditions. VCF is also a widely used parameter in membrane filtration studies [3, 21, 22]. It provides an advantage over using permeate volume by accounting for the change in physicochemical properties of the membrane due to the retained HA during filtration.

Fig. 1a shows the increase in flux for the UF-biochar process compared with the UF alone at varying biochar concentration and unstirred conditions; the flux decline followed the order no biochar $\geq$ 40 mg/L biochar > 20 mg/L biochar. This can be explained based on the properties of the biochar (Table 1) and the hydrodynamic condition. The biochar used in this study contained high aromaticity (74.1%), pore volume (micro- and macro-pore, 0.313 and 0.318 cm^3/g, respectively), and surface area (1151 m^2/g), which enhanced its adsorption of organic compounds, such as HA, leading to an increase in flux for the

11

process [23]. This is also evident under the stirred conditions (Fig. 1b) where the UF-biochar process with 40 mg/L biochar showed the highest flux followed by the process with 20 mg/L biochar. However, in the unstirred condition, a different trend occurred such that 40 mg/L showed a lower flux than 20 mg/L biochar, presumably because under unstirred conditions, such a high concentration of biochar, caused pore blockage and, consecutively, a lower flux. This can be substantiated further by the fact that the small pore size of the 5-kDa membrane used also leads to increased cake layer formation and, consequently, lower flux [24]. It is evident that the flux decline trend was similar for all three processes under stirred conditions, whereas a greater flux decline was noted due to increased pore blocking under unstirred conditions.

Fig. 1c and d shows the effects of biochar concentration on HA removal in the UF-biochar and UF-membrane processes. In comparing the data for the unstirred and stirred conditions, it is clear that the stirred condition showed approximately 12% greater HA rejection than the unstirred condition. However, under stirred conditions, the UF alone showed slightly higher rejection than the UF-biochar process. This can be explained by the occurrence of fouling due to concentration polarization in the initial stages, followed by membrane pore blocking and gel resistance [25]. Under unstirred conditions, the three processes showed similar rejection trends, while the process with 40 mg/L biochar showed a greater decline in rejection over the VCFs. In comparison, the UF alone and UF membrane with 20 mg/L biochar showed smaller declines in HA rejection. They also had similar removal efficiencies: approximately 85% for both the UF-biochar (20 mg/L) and UF alone processes. While a smaller flux decline and similar rejection trends were observed under unstirred conditions, this study focused on the UF-biochar process under

unstirred conditions for the remainder of this study, since previous studies have suggested that relatively less assumptions are necessary to evaluate membrane fouling resistance using the resistance-in-series model at unstirred conditions [26-28]. Additionally, the rejection rate for the UF-biochar process (40 mg/L) declined substantially over VCFs versus 20 mg/L biochar, presumably because the biochar at a high concentration may act as a foulant. Thus, 20 mg/L is considered a more optimum dose of biochar and the performance of UF membrane combined with 20 mg/L biochar was studied in the removal of HA under different water chemistry and operational conditions.

3.2. Effects of pH and conductivity

Various drinking water sources, such as ground/surface waters and wastewater effluents, being treated have complex compositions, and varying pH and conductivity levels. Thus, it is important to evaluate the effects of solution pH on HA. Fig. 2 shows the effects of pH on flux decline and HA rejection in the UF alone, and in the UF membrane combined with 20 mg/L biochar, as a function of VCF. Generally, the UF-biochar process showed a lower flux decline than the UF alone under all three pH conditions. Fig. 2a further shows that the process had the worst flux decline at pH 4, where the UF-biochar process showed a slightly higher flux (approximately 5%) than the UF alone. In comparison, the flux decline was much less at pH 7 and 10 than that at pH 4, while the UF-biochar process showed significantly higher flux (23.7%) than the UF alone at pH 7. Fig. 2b shows the HA rejection trends under different pH conditions. The UF-membrane-alone and the UF-biochar processes showed similar removal trends under different conditions. At pH 4, both the processes showed significantly higher removal than at pH 7 and 10. The higher rejection at pH 4 was also presumably due to the pore size reduction associated with

membrane fouling through HA concentration polarization at the membrane interface [2]. This was also observed in a previous study where, at lower pH, the rejection by UF membranes increased to 90–95% [18]. This may also explain the lower flux observed in Fig. 1a. In comparison, membrane fouling was found to be relatively low at the other pH values and thus the process showed a higher flux. Another reason for higher rejection at pH 4 is due to the fact that the negative charges on HA and the membrane surface become less negative at lower pHs, leading to a reduction in electrostatic repulsion between the two, thereby increasing adsorption and, consequently, the rejection rate [24].

The effects of solution conductivity on the flux decline and rejection trends, of the UF membrane process alone and the UF-biochar process, were observed under low and high conductivity conditions, 300 and 11,000 µS/cm, respectively (Fig. 3). Generally, it was observed that with high conductivity conditions, the flux decline was slightly greater than under low conductivity conditions. This trend toward flux decline with increasing conductivity may seem to be contrary to the flux decline trend with increasing pH. The UF alone showed a relatively high flux decline versus the UF-biochar process. Even in terms of rejection, the high-conductivity conditions showed a slightly lower percentage rejection (approximately 3.5%) than the no-salt conditions (Fig. 3b). Both the UF alone and UF-biochar process showed lower rejection under increased conductivity and pH conditions. In general, this can be explained by the fact that the effect of conductivity on adsorption onto biochar is pH-dependent. In the high-conductivity conditions, the negative charge on the biochar is neutralized by Na^+ ions, which reduce the electrical double layer near the surface, resulting in decreased electrostatic repulsion. This, in turn, increases the adsorption rates [23]. In this case, however, the increased conductivity did not increase the rejection

percentage, which may be attributable to the neutral pH conditions under which the experiment was conducted. This reduced the increased adsorption effect of biochar at higher ionic strengths. Another factor that may support the observed trend is that at high ionic strengths, the cake layer at the membrane surface becomes further compacted and leads to increased membrane fouling, which reduces the rejection by the UF and UF-biochar processes at high conductivity versus low conductivity conditions.

3.3. Membrane fouling resistance

The fouling layer characteristics associated with flux decline were evaluated using the resistance-in-series model in the presence of biochar under various water chemistry and operating conditions. Results of this analysis are summarized in Table 3. Unlike stirred conditions, where significantly lower fouling resistances were observed, comparable trends were obtained for the total fouling resistance in the UF-biochar and UF alone processes under unstirred conditions. Fouling resistance increased with the HA solution under unstirred conditions due to the formation of a cake/gel layer or concentration polarization layer. It is known that a concentration polarization layer significantly influences membrane resistance for flux decline in the concentration polarization-cake/gel layer model [20]. The results showed that the total fouling resistances clearly decreased in the presence of biochar, presumably due to HA adsorption onto the biochar (approximately 10% more HA adsorption in the UF-biochar than the UF process alone). The membrane inner pores and surface can be fouled readily by the high concentration of HA in the UF process alone, resulting in higher fouling resistance than in the UF-biochar process. The highest total fouling resistance (approximately 82×10^{12} 1/m) occurred at pH 4. However, in general, the fouling resistances decreased in the UF-biochar process under the same conditions,

because HA adsorption by biochar could considerably diminish the adsorptive fouling onto the UF membrane, resulting in lower HA compaction on the membrane and an insignificant fouling resistance increase in the UF-biochar process. In particular, the modeling results indicate that the adsorptive fouling resistance was much higher than the cake resistance, as indicated by the relatively low cake resistance ratio (R_c/R_t). These findings are consistent with previous research results on HA adsorption fouling with UF membranes [5, 29, 30].

3.4. Influence of pressure and effects of three-cycle test

Fig. 4 shows flux decline and HA rejection trends over different applied pressures for the UF-biochar and UF alone processes. Fig. 4a shows the normalized flux against VCF at 173, 345, and 690 kPa for the two processes. Generally, it can be seen that the flux decline was less with an increase in applied pressure. The reason for this trend remains unclear; however, one possible explanation is that at higher pressures, the cake layer formation at the membrane surface is reduced; allowing more permeate flow and thus increased flux. At 690 kPa, a significant increase in flux (74%) can be seen versus 173 kPa, and under all three applied pressures, the UF-biochar process showed a higher flux than the UF alone (25–29%). In Fig. 4b, rejection trends can be observed for UF-biochar and the UF alone at the same applied pressures. Under all three pressure conditions, UF-biochar showed a similar or slightly higher rejection trend than the UF alone. Both processes at 173 kPa showed slightly higher rejection (89.8%) than at 345 kPa (84.7%) and 690 kPa (84.2%). This trend is somewhat different from what has been observed in some previous studies on adsorbent UF membrane combined processes, where a significant decrease in rejection was noted (up to 50%) with increased pressure [3, 25, 31]. According to these studies, rejection decreased with increased pressure, because an increase in pressure would cause greater

16

dominant convective processes in NOM rejection. Back diffusion would not contribute significantly to NOM rejection because it was hindered by the stirring speed at which the experiments were conducted. In our study, the experiments were conducted under unstirred conditions and the effect of back diffusion could be more prominent, leading effectively to a lesser decrease in rejection with increased pressure.

Fig. 5 shows the normalized flux and rejection percentages for the UF-biochar and UF-membrane-alone processes over three filtration cycles. This helps compare the membrane recovery capabilities of both systems. As expected, flux declined considerably over the three cycles, with cycle 3 showing a 39–40% flux decline versus cycle 1. Neither the UF membrane nor the UF-biochar processes showed full flux recovery over subsequent filtration cycles, but the UF-biochar process showed a better flux recovery than the UF alone. The UF membrane showed higher flux decline due to increased membrane fouling over each filtration cycle. The UF-biochar process showed less flux decline, but some amount of flux decline was due to the presence of biochar residue on the membrane surface, which possibly hindered the thorough cleaning of the membrane with DI water before the subsequent filtration cycle. A similar trend was observed in previous studies with other adsorbents, such as PAC, coupled with UF membranes, indicating that PAC residue on the membrane hindered backwashing and the backwashing process was only efficient for adsorbent doses less than 20 mg/L [9].

Fig. 5b shows the rejection trends over subsequent cycles of filtration: there was an increase in rejection rates over the membrane in each membrane filtration cycle (3.1–4.7%). This trend can be seen clearly in the 3D plot shown in Fig. 6. The reason for this trend can be explained by the adsorption mechanisms discussed previously. The presence

of more HA near the membrane surface could lead to increased fouling with each cycle of filtration; thus, greater rejection and a greater flux decline was observed. In case of the UF-biochar process, this effect was relatively less pronounced due to the adsorption of some amount of HA by the biochar, which reduced fouling of the membrane and increased its recovery capacity, showing that the UF-biochar process had greater membrane recovery and antifouling capability than the UF alone.three cycles of filtration, with approximately 81–84%, 82–86%, and 84–88% rejection being observed over cycles 1, 2, and 3, respectively. Furthermore, the UF-biochar process showed better rejection performance than the UF
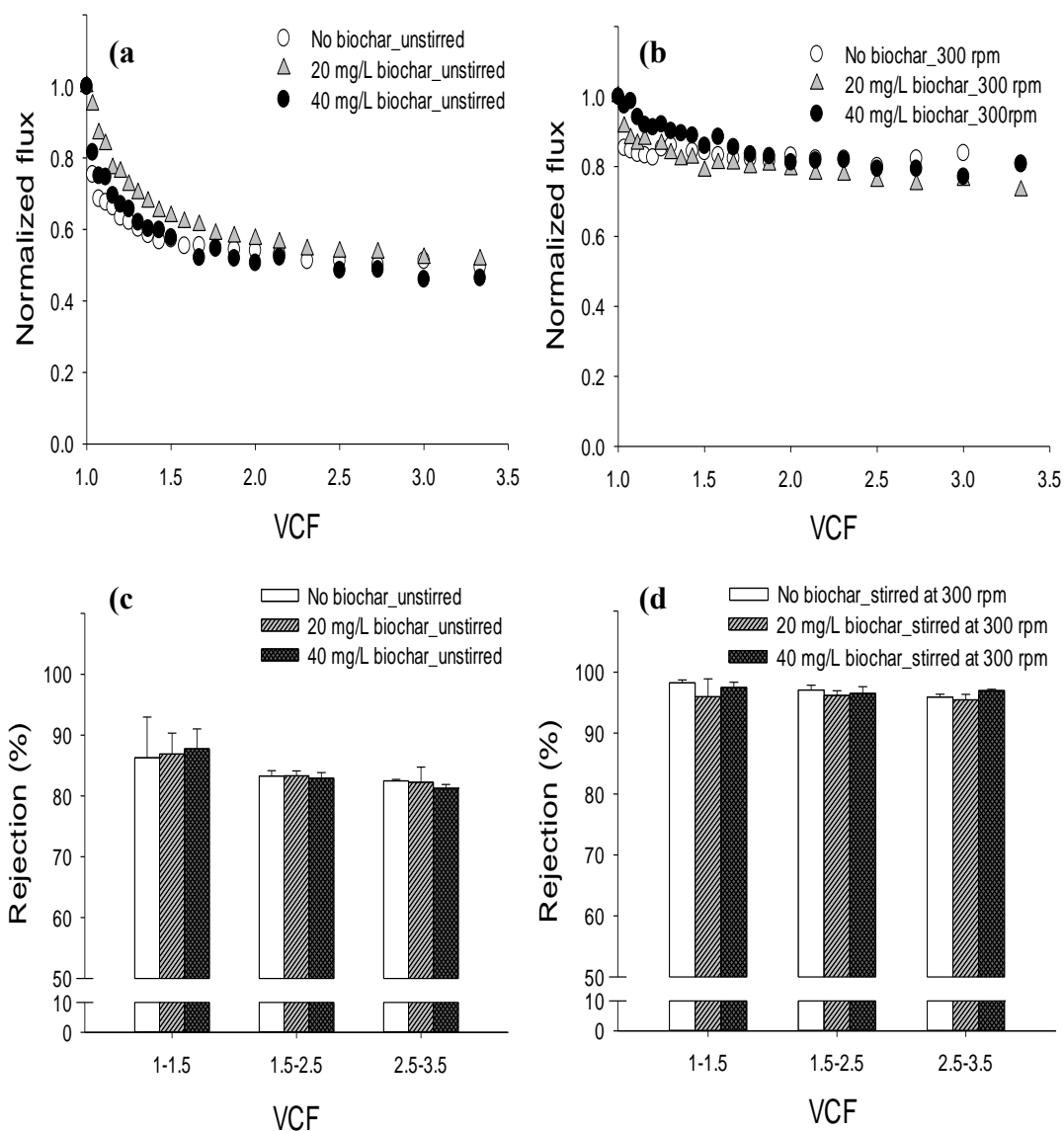
Figure 3.1 Influence of biochar concentration on flux decline and HA rejection as a function of biochar concentration for a UF membrane: (a) flux decline without stirring, (b) flux decline at 300 rpm, (c) HA rejection based on UVA_{254} without stirring, and (d) HA rejection based on UVA_{254} at 300 rpm. Operating conditions: $\Delta P = 345$ kPa (50 psi); DOC = 5 mg/L; biochar = 0, 20, and 40 mg/L; conductivity = 300 μS/cm; pH = 7; pre-contact time with biochar = 2 h
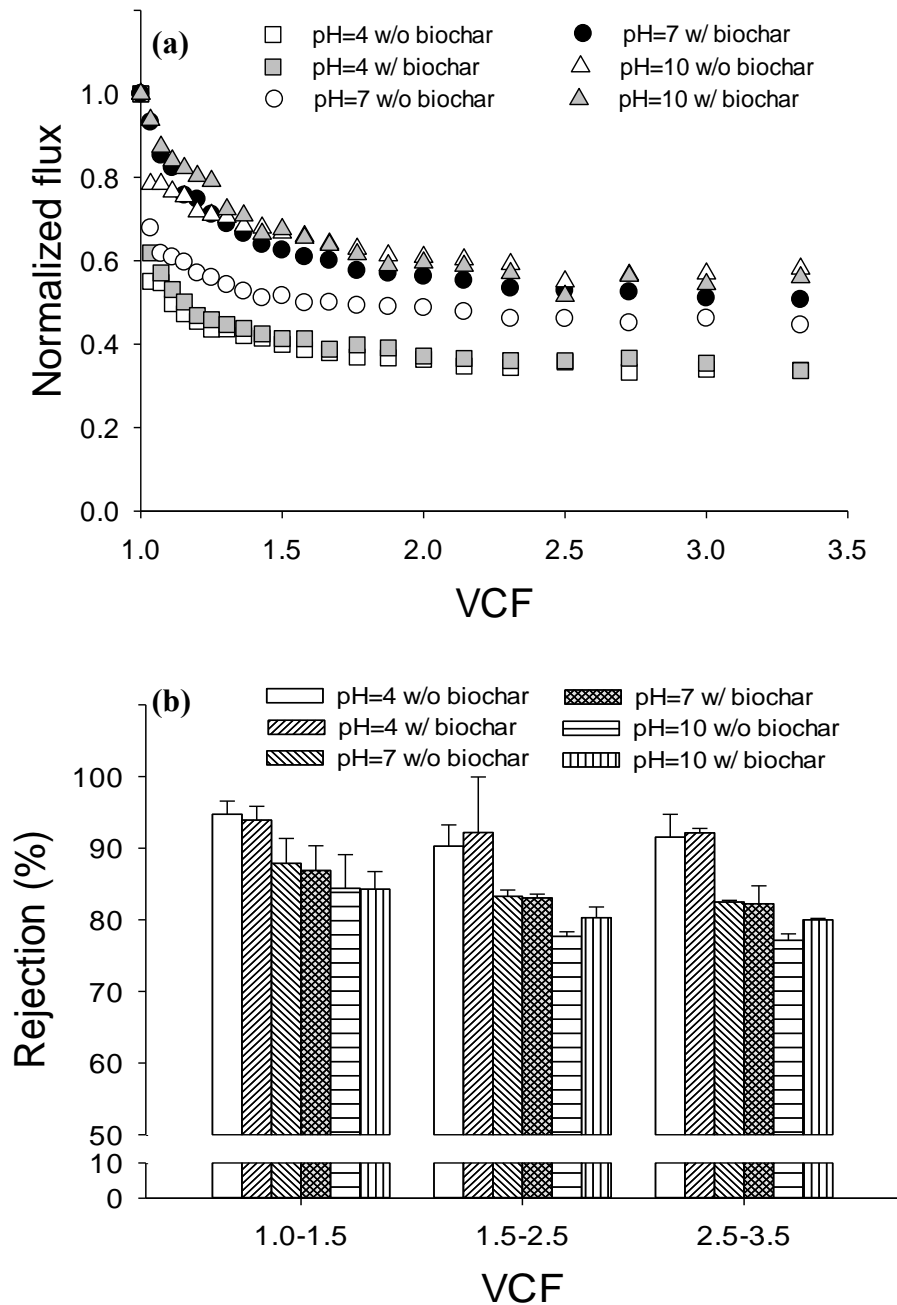
Figure 3.2. Influence of pH on flux decline and HA rejection based on DOC in the absence and presence of biochar: (a) normalized flux decline and (b) HA rejection based on DOC at different pH conditions. Operating conditions: $\Delta P = 345$ kPa (50 psi); DOC = 5 mg/L; biochar = 20 mg/L; conductivity = 300 µS/cm; pH = 7; pre-contact time with biochar = 2 h.
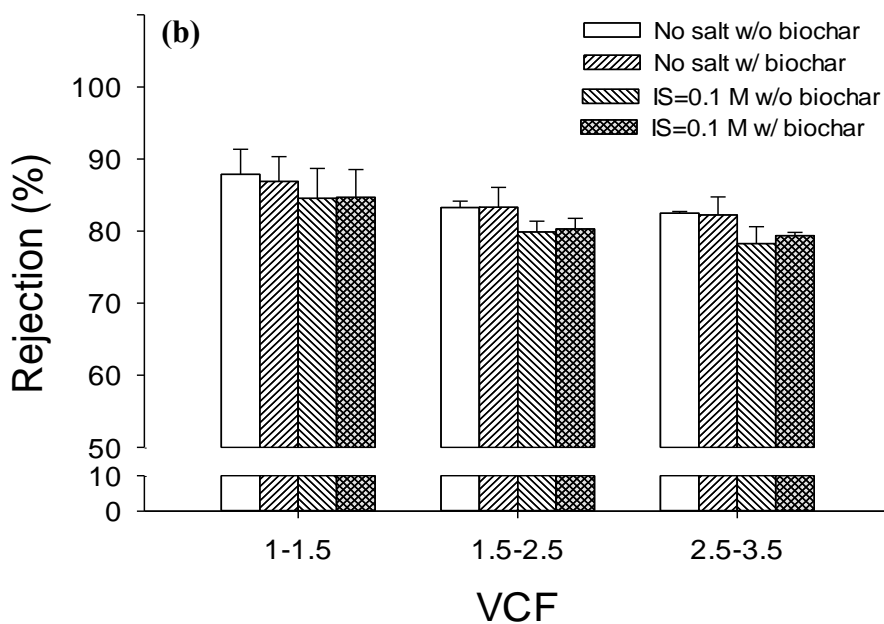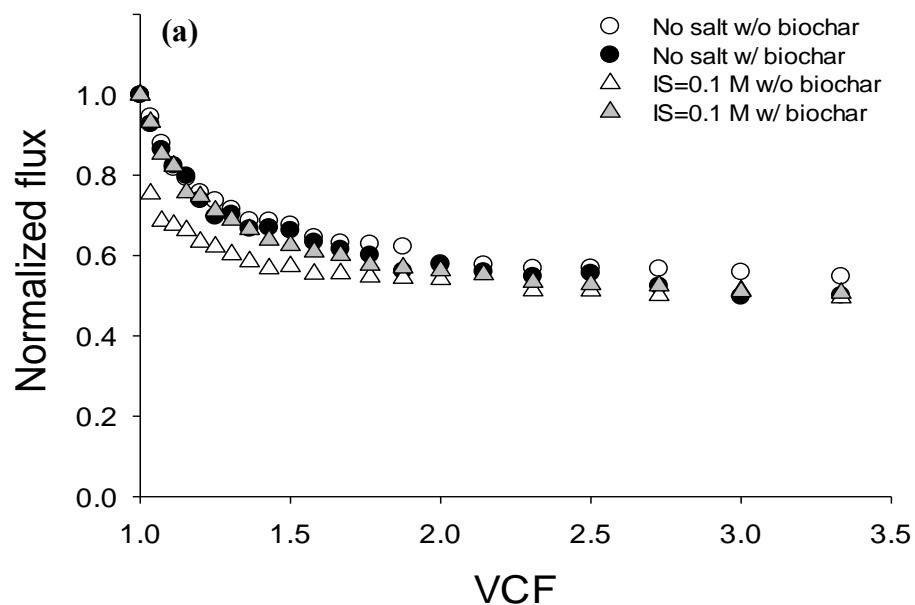
Figure 3.3. Influence of conductivity on flux decline and HA rejection based on DOC in the absence and presence of biochar: (a) normalized flux decline and (b) HA rejection based on DOC. Operating conditions: ΔP = 345 kPa (50 psi); DOC = 5 mg/L; biochar = 20 mg/L; low and high conductivity = 300 μS/cm and 11,000 μS/cm, respectively; pH = 7; pre-contact time with biochar = 2 h.
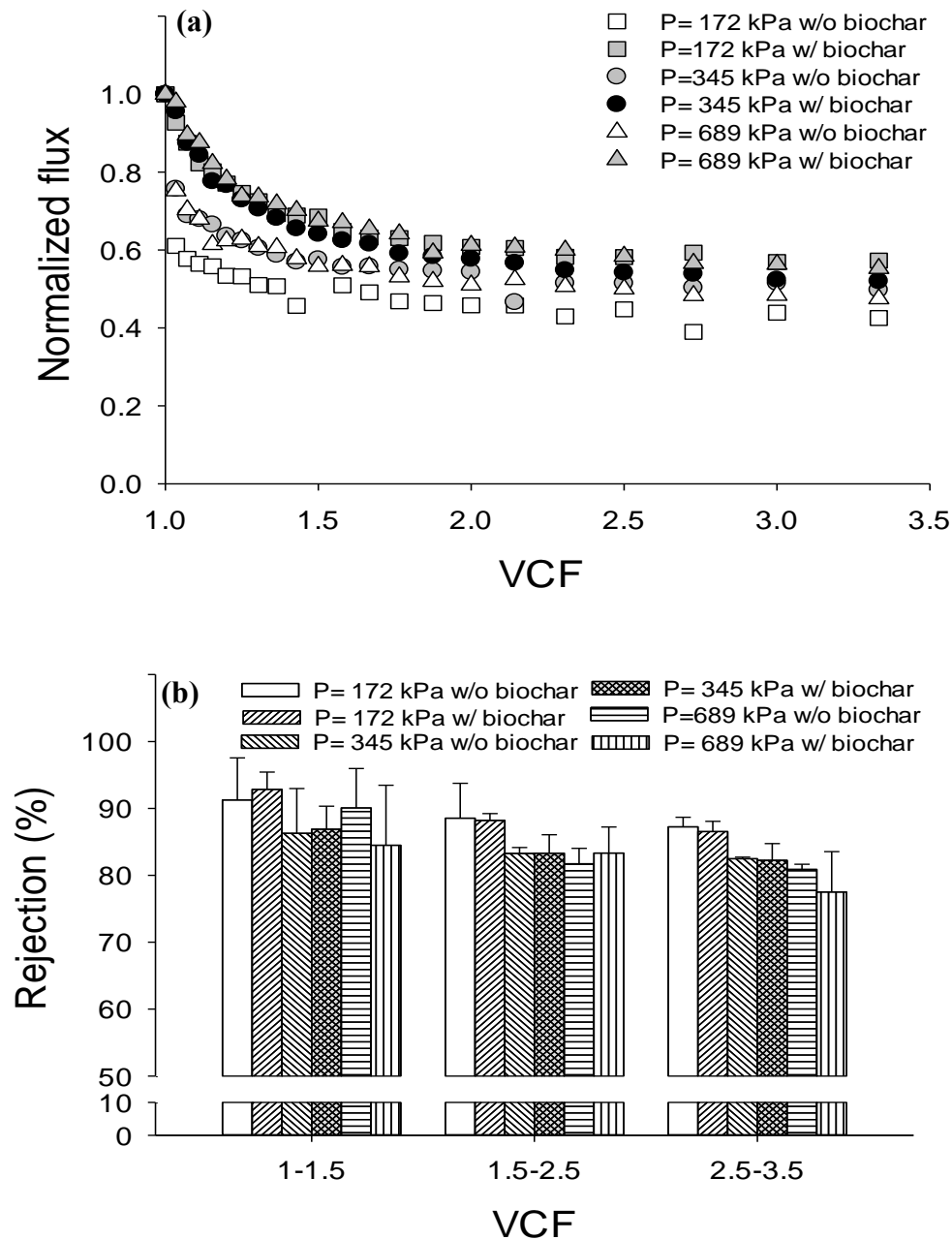
Figure 3.4. Influence of applied pressure on flux decline and HA rejection based on DOC in the absence and presence of biochar: (a) normalized flux decline and (b) HA rejection at different applied pressures. Operating conditions: $\Delta P = 173$ kPa (25 psi), 345 kPa (50 psi) and 690 kPa (100 psi); DOC = 5 mg/L; biochar = 20 mg/L; conductivity = 300 µS/cm; pH = 7; pre-contact time with biochar = 2 h.
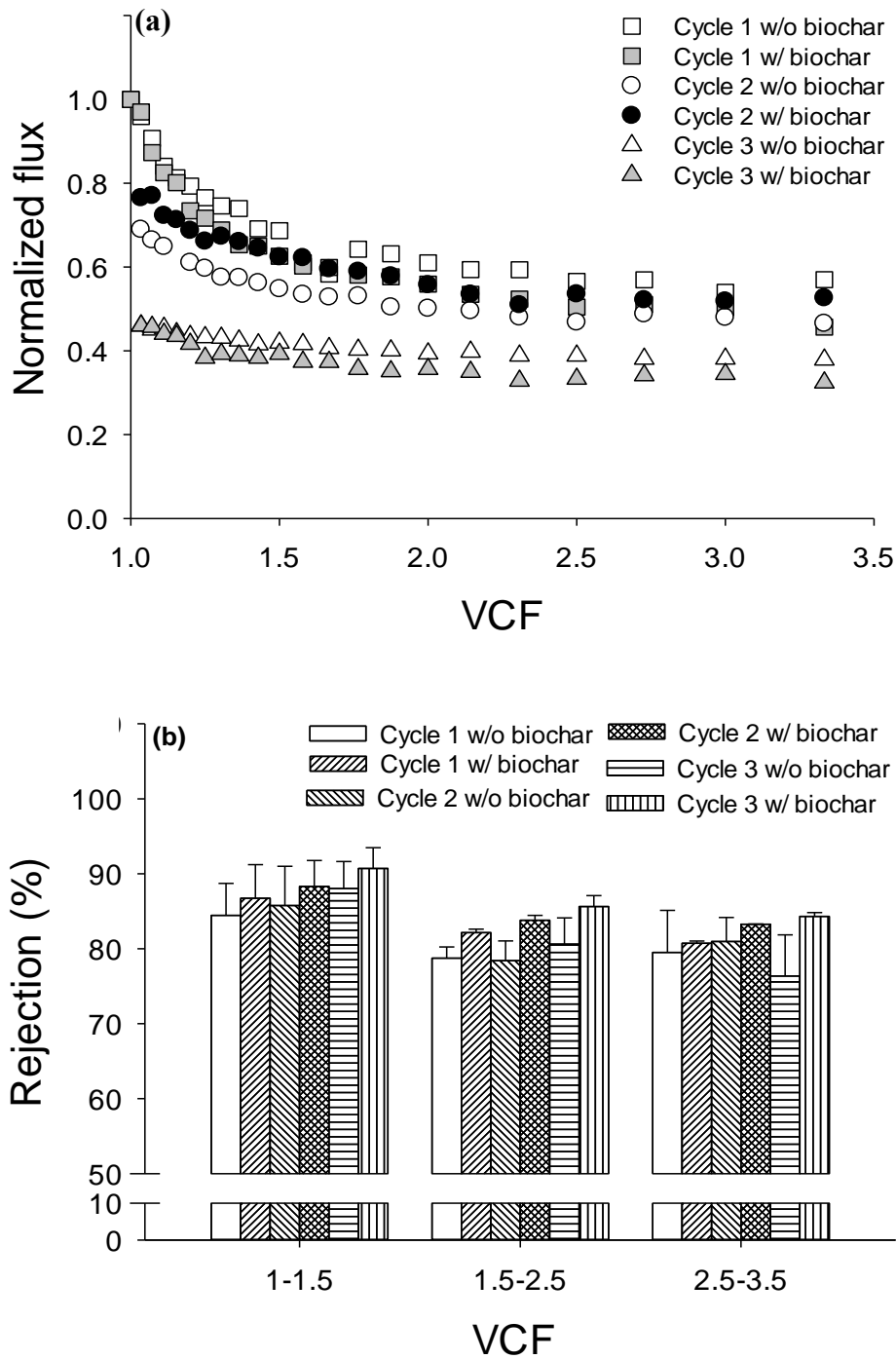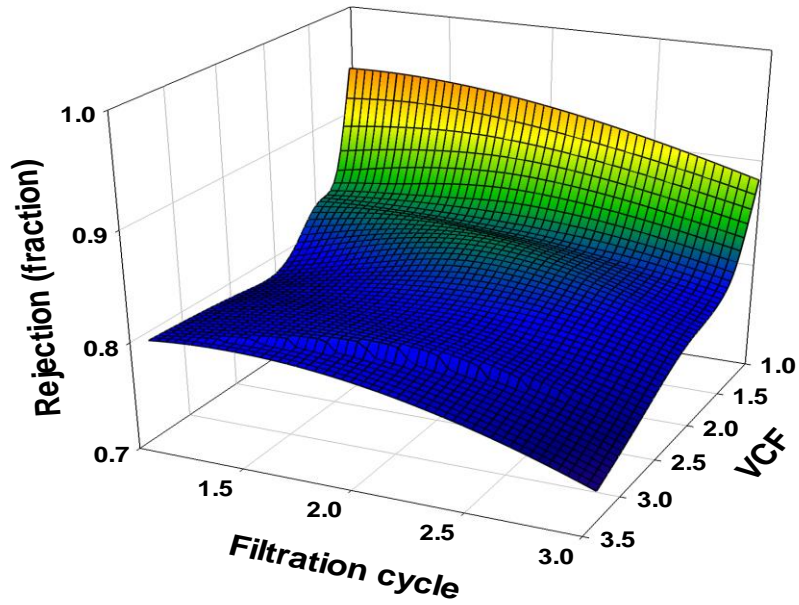
Figure 3.5. Influence of 3 cycles of filtration on flux decline and HA rejection based on DOC in the presence and absence of HA: (a) normalized flux decline and (b) HA rejection over 3 cycles of filtration. Operating conditions: ΔP = 345 kPa (50 psi); DOC = 5 mg/L; biochar = 20 mg/L; conductivity = 300 μS/cm; pH = 7; pre-contact time with biochar = 2 h.

(a) 3 cycle experiment without biochar
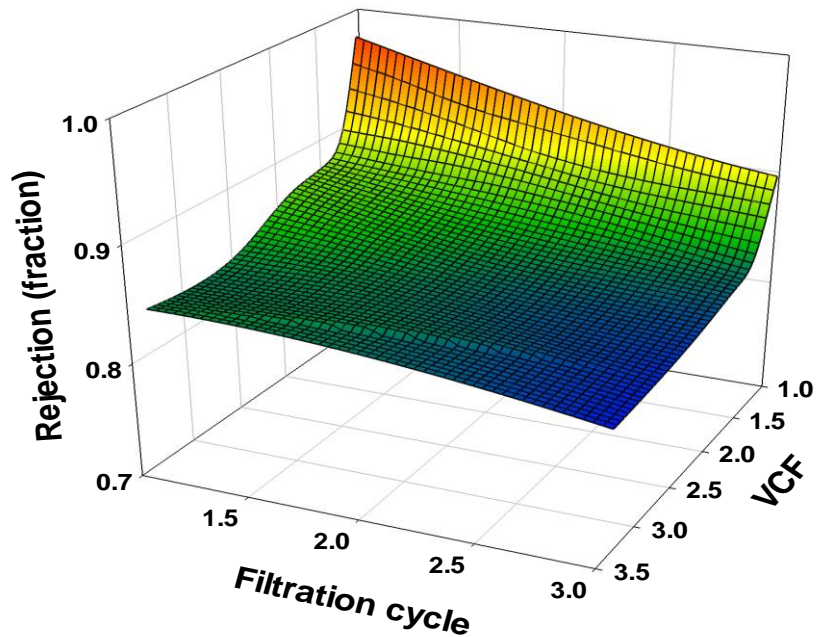

(b) 3 cycle experiment with biochar

Figure 3.6. Comparison of HA rejection trends with respect to cycle of filtration and VCF over 3 cycles of filtration (a) without biochar and (b) with biochar. Operating conditions: $\Delta P = 345$ kPa (50 psi); DOC = 5 mg/L; biochar = 20 mg/L; conductivity = 300 µS/cm; pH = 7; pre-contact time with biochar = 2 h.

Table 3.1. Characteristics of the fouling layer and resistances as a function of unit retained DOC mass in the absence and presence of biochar and various operating conditions according to resistance-in-series model.

Process	Solution & operating conditions			Characteristics of the fouling layer and resistances				
	TMP (kPa)	pH	IS	R_m (10^{12} m^{-1})	R_t (10^{12} m^{-1})	R_c (10^{12} m^{-1})	R_c/R_t	δ
UF	345	7.0	No salts	27.5	55.5	18.1	0.327	92.3
		7.0[*]		26.2	32.5	28.9	0.089	33.5
		4.0		27.7	82.0	14.8	0.181	177.7
		10.0		27.5	47.3	18.7	0.396	90.1
	345	7.0	0.1 M	27.5	55.5	23.1	0.417	92.2
	173	7.0	No salts	22.8	53.6	11.3	0.211	91.7
	690	7.0		27.4	57.7	10.5	0.182	95.6
Biochar-UF (40 mg/L)	345	7.0	No salts	24.4	52.7	21.2	0.402	85.9
Biochar-UF (20 mg/L)	345	7.0	No salts	27.1	52.3	15.5	0.296	91.2
		7.0[*]		21.0	28.7	51.0	0.178	31.8
		4.0		27.5	81.8	23.9	0.293	172.8
		10.0		23.9	42.8	18.1	0.424	89.5
	345	7.0	0.1 M	22.9	45.2	19.1	0.423	78.0
	173	7.0	No salts	22.3	38.9	10.1	0.260	64.0
	690	7.0		23.3	42.2	13.3	0.315	68.3

[*]stirring.

CHAPTER 4

CONCLUSIONS

In this study, we investigated the performance of an integrated process of a UF membrane with biochar, to improve the shortcomings of UF membranes alone in the treatment of challenging compounds, such as HA. It was found that hydrodynamic conditions strongly affected the performance of the processes, with UF-biochar showing similar removal but higher flux than the UF alone under unstirred conditions of operation versus stirred conditions, where the UF membrane showed slightly better rejection and similar flux to UF-biochar. Then, we focused on the unstirred condition of operation and the performances of the two processes were evaluated at various pH and conductivity levels. At pH 4, UF-biochar showed significantly higher rejection and subsequently higher flux decline than at pH 7 and 10, which was attributed to concentration polarization occurring at the lower pH level. UF-biochar showed better flux and similar or higher rejection than the UF alone under all three pH conditions. Regarding conductivity, better flux was observed at lower than at higher conductivity and UF-biochar performed better. Both the UF alone and UF-biochar processes showed less rejection with increasing conductivity and pH. To understand the complete working of the processes, another important aspect such as membrane recovery was analyzed for both processes, and UF-biochar showed better recovery and less flux decline after three cycles of filtration. This helped establish that integration of biochar with the UF

membrane treatment technology hindered membrane fouling to some extent and improved

the treatment of NOM like HA. Although future studies still need to explore the exact

mechanisms of the treatment processes, this study demonstrated that an integrated process

with UF-biochar may be useful for future applications in the treatment of NOM.

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