

# The Targeted Removal of Dissolved Organic Matter in Boiler Blowdown Wastewater: Integrated Membrane Filtration for Produced Water Reuse

*Gil Hurwitz<sup>1,\*</sup>, David J. Pernitsky<sup>2</sup>, Subir Bhattacharjee<sup>1</sup>, and Eric M.V. Hoek<sup>1</sup>*

<sup>1</sup>Water Planet, Inc., 721 Glasgow Ave, Unit D; Los Angeles, California, USA

<sup>2</sup>Suncor Energy Inc., P.O. Box 2844, 150 Sixth Avenue SW, Calgary AB, T2P 3E3 Canada

Industrial & Engineering Chemistry Research

\* Corresponding author: Tel: (424) 331-7706; Fax: (424) 331-7799; E-mail:  
gil@waterplanet.com

## Supporting Information

### Velocity gradient calculations

RMS velocity gradients,  $\bar{G}$ , were calculated using the following equation:

$$\bar{G} = \sqrt{\frac{\bar{\varepsilon}}{\nu}} \quad (1)$$

where  $\nu$  is the fluid kinematic viscosity [ $\text{m}^2/\text{s}$ ] and  $\bar{\varepsilon}$  is the average energy dissipation [ $\text{m}^2/\text{s}^3$ ].

The average energy dissipation was dependent on the mixing apparatus as well as the flow conditions within the vessel.<sup>1,2</sup> Klöckner et al. and others have derived the following equations to calculate the power input and average energy dissipation for a shaker reactor, as was used in the preliminary coagulation jar tests:<sup>3-5</sup>

$$\bar{\varepsilon} = \frac{P}{V_L \cdot \rho} \quad (2)$$

$$Re = \frac{\rho \cdot n \cdot d^2}{\mu} \quad (3)$$

$$Ne' = 70Re^{-1} + 25Re^{-0.6} + 1.5Re^{-0.2} = \frac{P}{\rho \cdot n^3 \cdot d^4 \cdot V_L^{1/3}} \quad (4)$$

where  $Re$  is the Reynolds number within the shaker vessel,  $Ne'$  is the modified Newton number,  $P$  is the power input [ $\text{kg} \cdot \text{m}^2/\text{s}^3$ ],  $V_L$  is the liquid volume within the shaker vessel [ $\text{m}^3$ ],  $\rho$  is the fluid density [ $\text{kg}/\text{m}^3$ ],  $n$  is the shaking/mixing frequency [ $\text{s}^{-1}$ ],  $d$  is inner diameter of the cylindrical mixing vessel [ $\text{m}$ ], and  $\mu$  is the fluid dynamic viscosity [ $\text{kg}/\text{m} \cdot \text{s}$ ]. Preliminary coagulation jar tests were operated with the following conditions: orbital shaker reactor with 45 mL liquid volume, 25 mm inner tube diameter, and shaking frequencies of 200 rpm and 1000 rpm during slow and fast mixing stages, respectively. Slow mix coagulation resulted in a Reynolds number of 5900, power input of  $2.08 \times 10^{-4} \text{ kg} \cdot \text{m}^2/\text{s}^3$ , and RMS velocity gradient of  $115 \text{ s}^{-1}$ . Fast mix resulted in a Reynolds number of 29,500, power input of  $1.56 \times 10^{-2} \text{ kg} \cdot \text{m}^2/\text{s}^3$ , and

RMS velocity gradient of  $990 \text{ s}^{-1}$ .

In-line coagulation/filtration tests utilized a more traditional stirred mixing vessel equipped with a magnetic, cylindrical stir bar with a diameter of 22 mm. The RMS velocity gradient was calculated using Equations (1) and (2) and the power input was calculated from the following expression:

$$P = N_p \cdot n^3 \cdot D^5 \rho \quad (5)$$

where  $N_p$  is the dimensionless power number and  $D$  is the diameter of the stir bar [m]; other variables have been defined previously. The power number for magnetic stir bars has been defined from previous studies as 1.2, which resulted in a Reynolds number of 15,900, power input of  $9.6 \times 10^{-3} \text{ kg-m}^2/\text{s}^3$ , and RMS velocity gradient of  $300 \text{ s}^{-1}$ .<sup>4, 6</sup>

## References

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## Tables

**Table S1.**

The effect of in-line coagulation and pH on dissolved organic carbon (DOC) and conductivity rejection by a 720 Da MWCO nanofiltration membrane in dead-end mode at room temperature.

Sample	BBD Source	Applied Pressure (bar)	pH	Conductivity (mS/cm)	Cond. Rejection (%)	DOC (ppm C)	DOC Rejection (%)
Unadjusted BBD: Feed	Plant 1	10.3	11.9	13.5	–	2410	–
Unadjusted BBD: Permeate			12.0	8.11	39.9	363	84.9
Unadjusted BBD: Feed	Plant 2	14.8	11.6	33.7	–	5160	–
Unadjusted BBD: Permeate			11.5	16.4	51.3	790	84.7
Unadjusted BBD: Feed	Plant 3	27.4	12.2	59.4	–	2490	–
Unadjusted BBD: Permeate			12.2	38.1	35.8	243	90.2
BBD + 1000 ppm PAC (85 ppm Al): Feed	Plant 1	11.4	11.6	13.1	–	2510	–
BBD + 1000 ppm PAC (85 ppm Al): Permeate			11.6	6.87	47.6	375	85.1
BBD + 1000 ppm PAC (85 ppm Al): Feed	Plant 2	16.2	10.4	34.8	–	4960	–
BBD + 1000 ppm PAC (85 ppm Al): Permeate			10.4	16.7	52.0	715	85.6

BBD + 1000 ppm PAC (85 ppm Al): Feed	Plant 3	20.0	11.6	59.1	–	2350	–
BBD + 1000 ppm PAC (85 ppm Al): Permeate			11.6	40.5	31.5	266	88.7
BBD (pH <sub>o</sub> = 8): Feed	Plant 1	17.9	8.0	13.8	–	2580	–
BBD (pH <sub>o</sub> = 8): Permeate			7.7	5.18	62.5	310	88.0
BBD (pH <sub>o</sub> = 8): Feed	Plant 2	21.7	8.0	35.2	–	4800	–
BBD (pH <sub>o</sub> = 8): Permeate			8.0	14.8	57.9	605	87.4
BBD (pH <sub>o</sub> = 8): Feed	Plant 3	41.4*	8.0	59.4	–	2400	–
BBD (pH <sub>o</sub> = 8): Permeate			8.0	28.5	52.0	218	90.9
BBD (pH <sub>o</sub> = 4): Feed	Plant 1	24.1	4.0	15.1	–	1820	–
BBD (pH <sub>o</sub> = 4): Permeate			4.5	4.46	70.5	1000	45.0
BBD (pH <sub>o</sub> = 4): Feed	Plant 2	37.9	4.0	38.6	–	3270	–
BBD (pH <sub>o</sub> = 4): Permeate			4.0	8.4	78.2	1380	57.8
BBD (pH <sub>o</sub> = 4): Feed	Plant 3	30.3	4.1	61.6	–	1130	–
BBD (pH <sub>o</sub> = 4): Permeate			4.2	31.2	49.4	633	44.0

\*Note: The sudden loss in membrane permeability observed during the filtration of BBD from Plant 3 with initial pH adjusted to 8 resulted in operation at the maximum allowable pressure as recommended by the membrane manufacture, which was reached before the desired initial flux of 30 LMH could be attained.

## Supporting Figure Captions

### Figure S1

The effect of initial pH on coagulation efficiency for Plant 1 BBD using the following coagulant doses: (a) Acidification only, (b) 269 ppm generic alum (42.5 ppm Al), (c) 538 ppm generic alum (85 ppm Al), (d) 2692 ppm alum (425 ppm Al), (e) 500 ppm commercial PAC (42.5 ppm Al), (f) 1000 ppm commercial PAC (85 ppm Al), and (g) 5000 ppm commercial PAC (425 ppm Al). Note: From left to right, each sample set had an initial pH of 11.9, 8.0, and 4.0.

### Figure S2

The effect of initial pH on coagulation efficiency for Plant 2 BBD using the following coagulant doses: (a) Acidification only, (b) 269 ppm generic alum (42.5 ppm Al), (c) 538 ppm generic alum (85 ppm Al), (d) 2692 ppm alum (425 ppm Al), (e) 500 ppm commercial PAC (42.5 ppm Al), (f) 1000 ppm commercial PAC (85 ppm Al), and (g) 5000 ppm commercial PAC (425 ppm Al). Note: From left to right, each sample set had an initial pH of 11.6, 8.0, and 4.0.

### Figure S3

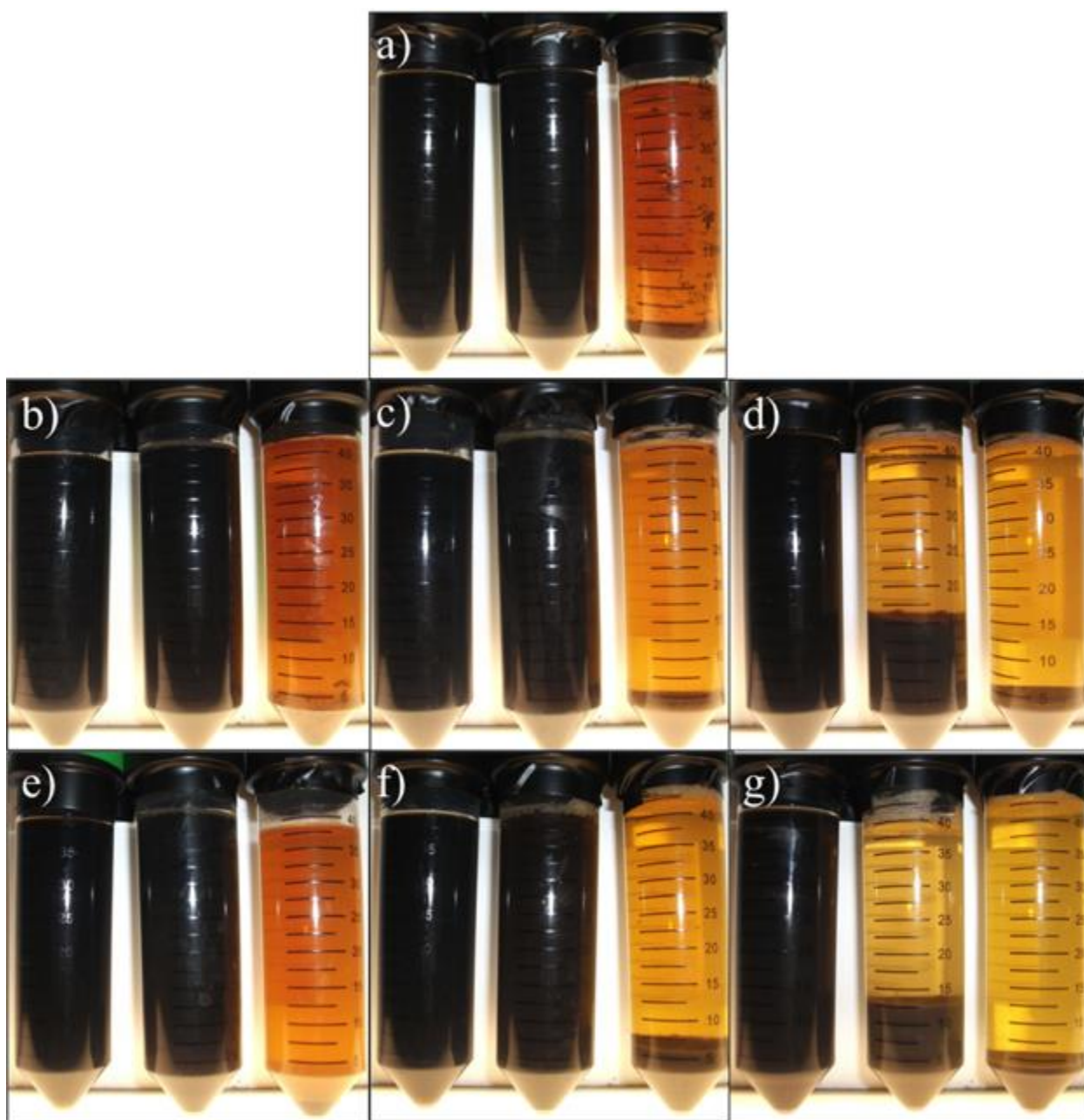
The effect of initial pH on coagulation efficiency for Plant 3 BBD using the following coagulant doses: (a) Acidification only, (b) 269 ppm generic alum (42.5 ppm Al), (c) 538 ppm generic alum (85 ppm Al), (d) 2692 ppm alum (425 ppm Al), (e) 500 ppm commercial PAC (42.5 ppm Al), (f) 1000 ppm commercial PAC (85 ppm Al), and (g) 5000 ppm commercial PAC (425 ppm Al). Note: From left to right, each sample set had an initial pH of 12.2, 8.0, and 4.0.

### Figure S4

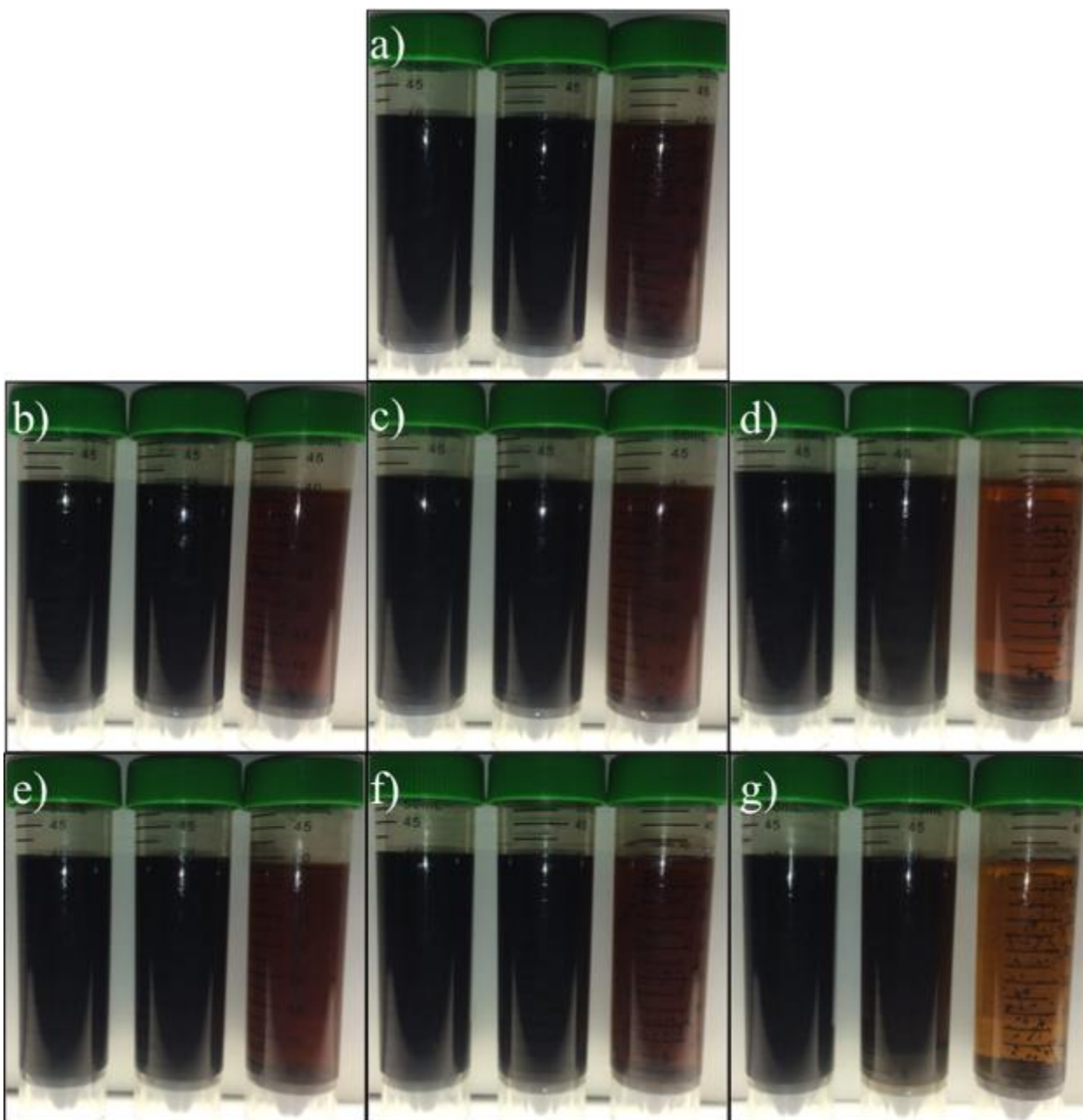
The effect of in-line coagulation and pH on membrane fouling during filtration of BBD from (a-d) Plant 1, (e-h) Plant 2, and (i – l) Plant 3 using a 720 Da MWCO NF membrane in dead-end mode at room temperature. Pretreatment consisted of (a, e, & i) no pretreatment, (b, f, & j) in-line coagulation with 1000 ppm commercial PAC, (c, g, & k) acidified BBD to pH 8, and (d, h, & l) acidified BBD to pH 4.

### Figure S5

720 Da MWCO nanofiltration membrane coupons after filtration of unadjusted BBD from (a) Plant 1, (b) Plant 2, and (c) Plant 3 in cross flow mode at constant pressure and 70 °C.

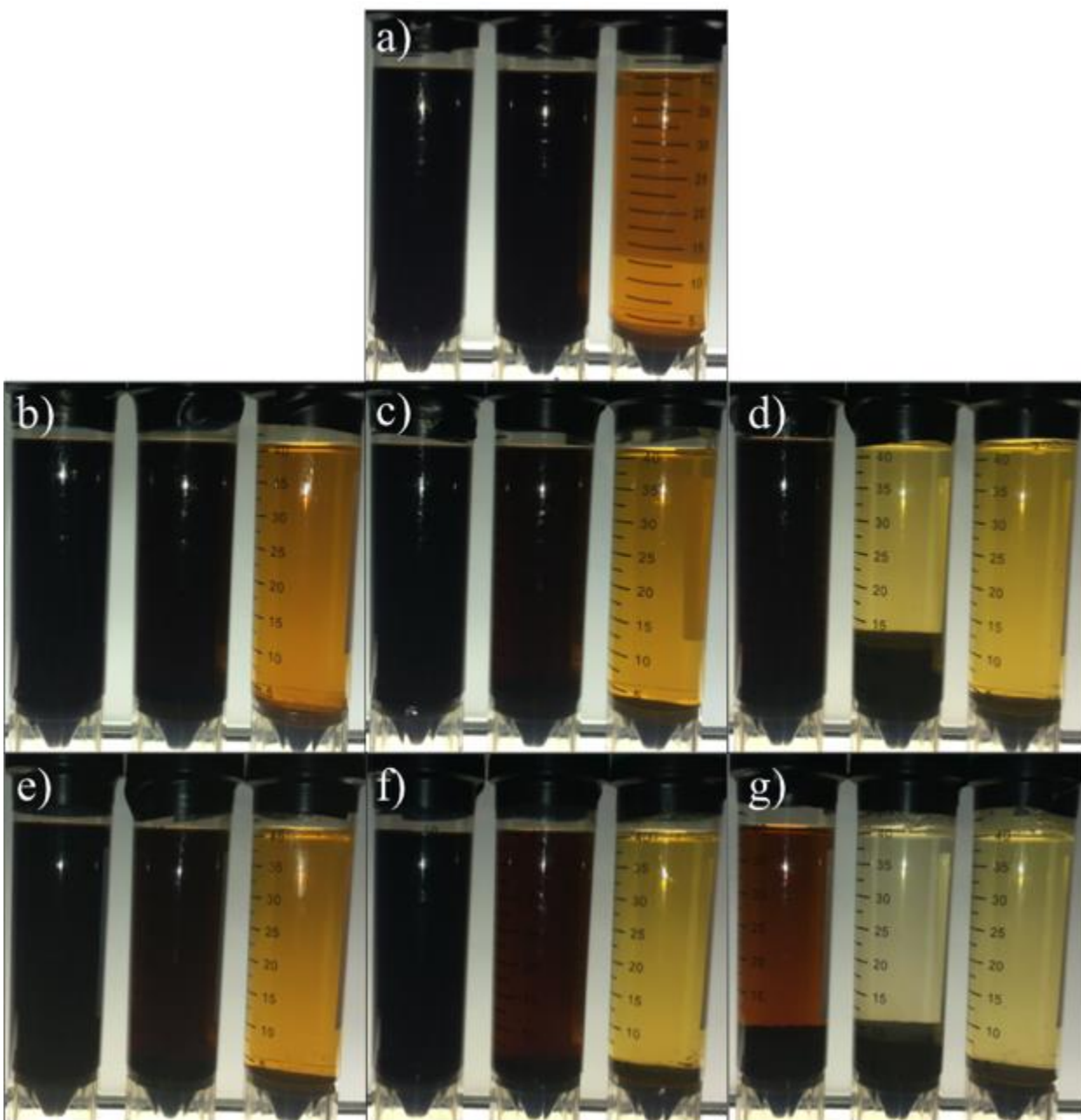


**Figure S1.** The effect of initial pH on coagulation efficiency for Plant 1 BBD using the following coagulant doses: (a) Acidification only, (b) 269 ppm generic alum (42.5 ppm Al), (c) 538 ppm generic alum (85 ppm Al), (d) 2692 ppm alum (425 ppm Al), (e) 500 ppm commercial PAC (42.5 ppm Al), (f) 1000 ppm commercial PAC (85 ppm Al), and (g) 5000 ppm commercial PAC (425 ppm Al). Note: From left to right, each sample set had an initial pH of 11.9, 8.0, and 4.0.

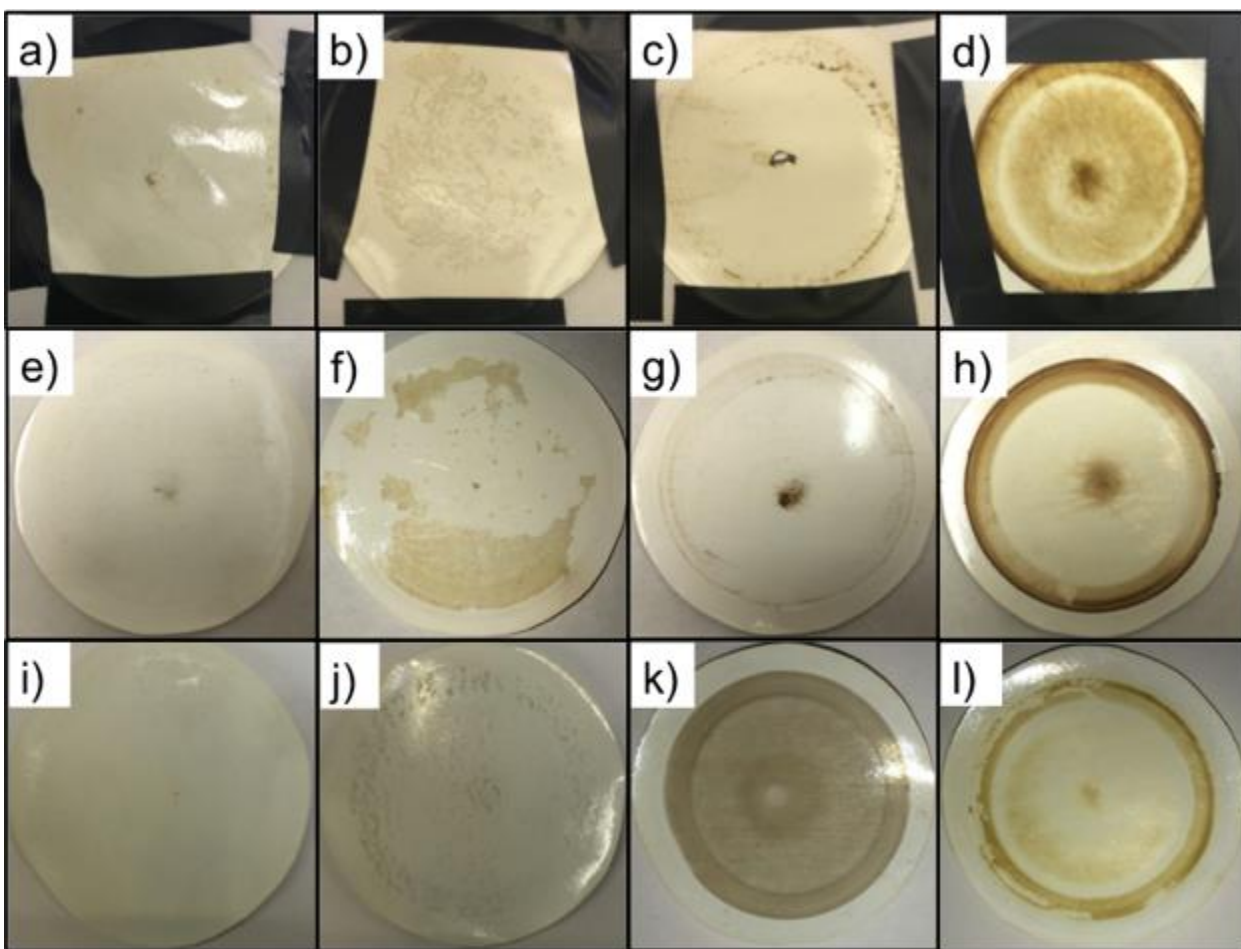


**Figure S2.** The effect of initial pH on coagulation efficiency for Plant 2 BBD using the following coagulant doses: (a) Acidification only, (b) 269 ppm generic alum (42.5 ppm Al), (c) 538 ppm generic alum (85 ppm Al), (d) 2692 ppm alum (425 ppm Al), (e) 500 ppm commercial PAC (42.5 ppm Al), (f) 1000 ppm commercial PAC (85 ppm Al), and (g) 5000 ppm commercial PAC (425 ppm Al). Note: From left to right, each sample set had an initial pH of 11.6, 8.0, and 4.0.

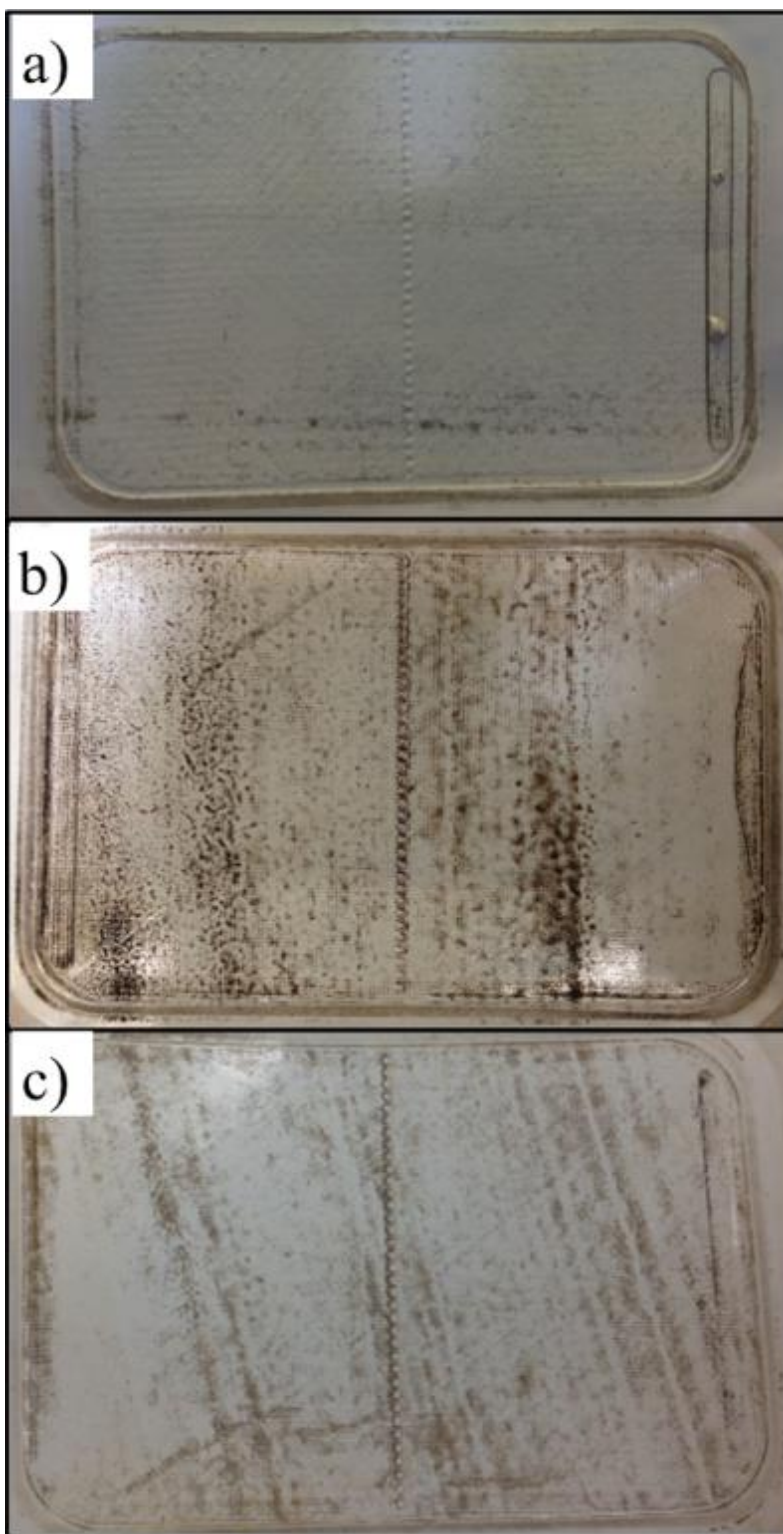




**Figure S3.** The effect of initial pH on coagulation efficiency for Plant 3 BBD using the following coagulant doses: (a) Acidification only, (b) 269 ppm generic alum (42.5 ppm Al), (c) 538 ppm generic alum (85 ppm Al), (d) 2692 ppm alum (425 ppm Al), (e) 500 ppm commercial PAC (42.5 ppm Al), (f) 1000 ppm commercial PAC (85 ppm Al), and (g) 5000 ppm commercial PAC (425 ppm Al). Note: From left to right, each sample set had an initial pH of 12.2, 8.0, and 4.0.



**Figure S4** The effect of in-line coagulation and pH on membrane fouling during filtration of BBD from (a-d) Plant 1, (e-h) Plant 2, and (i – l) Plant 3 using a 720 Da MWCO NF membrane in dead-end mode at room temperature. Pretreatment consisted of (a, e, & i) no pretreatment, (b, f, & j) in-line coagulation with 1000 ppm commercial PAC, (c, g, & k) acidified BBD to pH 8, and (d, h, & l) acidified BBD to pH 4.



**Figure S5** 720 Da MWCO nanofiltration membrane coupons after filtration of unadjusted BBD from (a) Plant 1, (b) Plant 2, and (c) Plant 3 in cross flow mode at constant pressure and 70 °C.