ISEH 2021

A pilot scale study for semiconductor wasewater reuse and ultrapure water production

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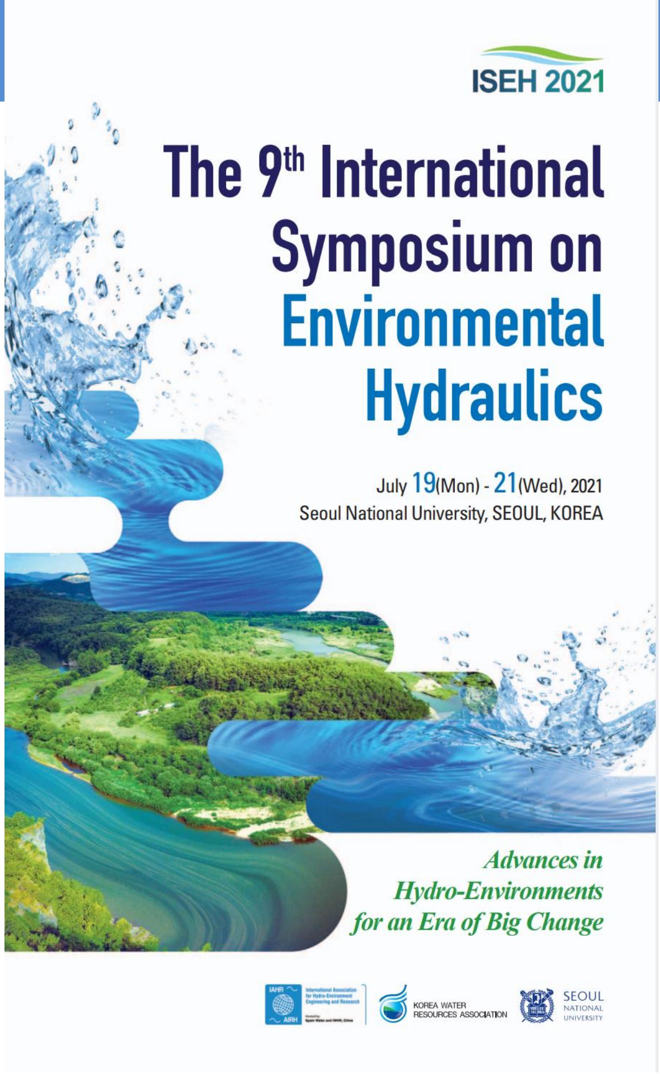


Day 1_Technical Program

Mini-symposium S2-M2 Hydro-environment in Cities-Water Cycle, Metabolism and Management

Chair: Yongju Choi (SNU)

S2-1
14:50-15:05
Feasibility of waste heat recovery from sewage in metropolitan cities
Jinsung An

S2-2
15:05-15:20
A pilot scale study for semiconductor wastewater reuse and ultrapure water production
Chong Min Chung

S2-3
15:20-15:35
Stochastic approaches for risk and resilience of groundwater systems under uncertainty
Jinwoo Im

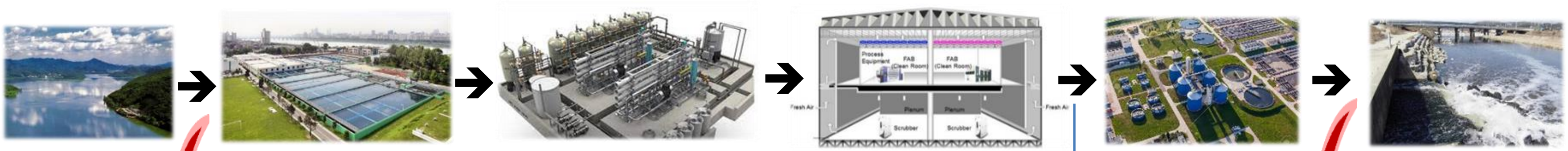
S2-4
15:35-15:50
Development and application of a polar organic chemical integrative sampler (POCIS) for monitoring micropollutants in a drinking water treatment plant
Hyun-ah Kwon, Yongju Choi

S2-5
15:50-16:05
Oxidation of aldehydes found in finished recycled wastewater with heterogeneous transition metal catalysts and dissolved oxygen
Euna Kim, Georgia Cardosa, Daniel L. McCurry

S2-6
15:50-16:05
Development of sensor technologies for smart water quality management in future cities
Jong Kwon Choe, Junyoung Park

1. Introduction

[Water flow in semiconductor manufacturing facility]



Water source → Water purification plant → Ultra pure water system → Fabrication → Wastewater plant → River discharge

◎ Ultrapure water(UPW) ◎ Cooling water
◎ Process water ◎ Sanitary water

◎ Organic, acids, ammonia-rich, fluoride-rich wastewater etc.

▣ Depletion of high-quality water resources

- A river : TOC 10,000 ppb
  LMW(total) 1,500 ppb
  Urea 250 ppb,
  B 0.1 ppb

▣ Reinforcement of industrial wastewater discharge standards

- COD_{mn} → TOC (2021~)
- Integrated pollution Prevention and Control Directive (2021~)
  - TN in effluent 20ppm →10ppm
- TDS(Sulfate & chloride ions) regulation

1. Introduction

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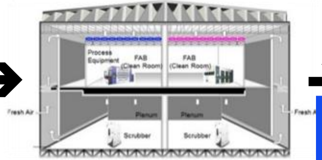
[Water flow in semiconductor manufacturing facility including a wastewater reuse system]


Water source


Water purification plant


Ultra pure water system



Fabrication


Wastewater plant


River discharge

Influent 100,000 ton/day reduction

100,000 ton/day of Wastewater reuse system

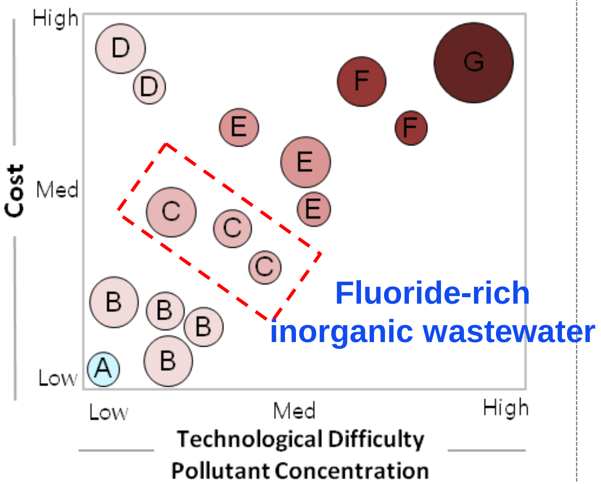
Discharge 100,000 ton/day reduction

- Enhancing the company's ecofriendly image
- Environmental regulations compliance
- Response to reinforcement of effluent regulations
- Ensure stable water resource quality and supply

Development procedure of wastewater recycle technology

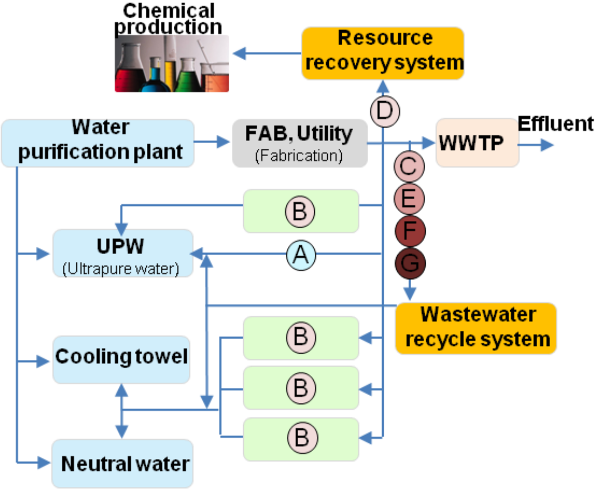
① Identifying the types of wastewater
(Water quality map)

- Selecting target wastewater
 (Low-level to High-level of pollutants)
 . A > B > C > D > E > F > G

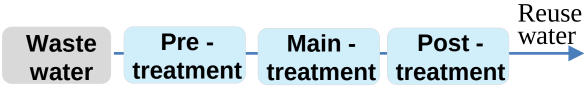


② Selecting the users of the reuse water
(Water balance map)

- Water quality and amounts required by users
 . UPW : TOC < 100ppb, Urea < 10ppb
 . Cooling water : TOC < 5ppm, Ca^{2+} < 5ppm
 . Neutral water : TOC < 2ppm, Ca^{2+} < 10ppm



③ Designing the reuse system



- A : Reuse without treatment
- B : Reuse with 3 stage treatment
- C : Reuse with 4 stage treatment
- D : Resource recovery from wastewater

Physical	Chemical	Electro-chemical	Biological
Activated carbon filtration	Advanced oxidation	Electro Oxidation	Aerobic
Sedimentation	Coagulatio/ Flocculation	Electro Coagulation	Anoxic
Flotation	Disinfection	Electro Flotation	Anaerobic
Membrane Filtration	Oxidation	Capacitive deionization (CDI)	MBR
Air stripping	Breakpoint chlorination	Electrodialysis (ED)	BAC (Biological activated carbon)

2. Materials &Methods

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Table 1. Compositions of the Fluoride-rich inorganic wastewater

Parameter	Influent	Parameter	Influent
pH	2.2	Na	15.6
Conductivity	4,505	Al	0.018
SS	4.1	Fe	0.289
VSS	0.7	Mn	0.008
TOC	5.8	W	25.8
COD_{cr}	63.7	Zn	0.209
T-N	13.1	T-Si	15.7
NH_3-N	11.4	Ionic-Si	14.3
T-P	0.3	Acetaldehyde	0.947
PO_4-P	0.1	Nitromethane	0.182
F	542	Methanol	0.846
Cl	8.4	Ethanol	1.678
SO_4	408	Acetone	0.697
Ca	0.33	IPA	0.995
Mg	0.06	Acetonitrile	0.142

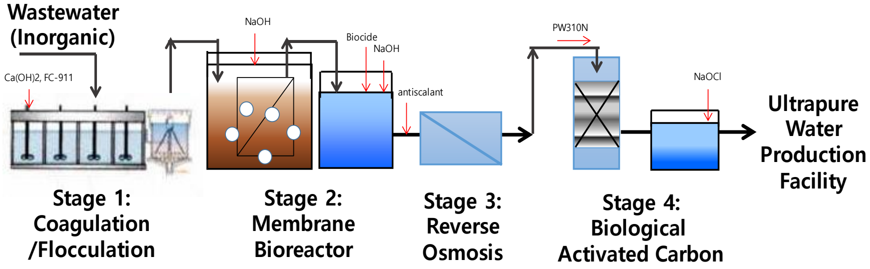
Target water quality :

Feed water for UPW production facility

- **TOC < 100 ppb**
- Urea < 10 ppb
- Turbidity < 0.2 NTU
- Conductivity < 130 μS/cm
- T-N < 4 ppm
- T-P < 0.2 ppm
- B < 0.1 ppm

2. Materials &Methods

Fig. 1. The four-stage wastewater reuse system



Stage 1	Value
Capacity	200 m^3/h
Chemical agents	$Ca(OH)_2$, PAC, Polymer
Stoichiometric molar ratio	$[Ca^{2+}]/[F^-]$ of 0.7
pH	7± 0.1

Stage 2	Value
Capacity	1.7 m^3/h
Membrane	PVDF hollow fiber UF membrane
Membrane area	94.8 m^2(net flux at 18 LMH)
Internal recycle	200%
operation cycle	Filtration: 14.5 min, Pause 30 sec
HRT	8 hr
Operation Condition	(a) Normal, (b) high TOC loading, (c) Low TOC loading

Stage 3	Value
Capacity	0.72 m^3/h
Membrane	Polyamide RO
Membrane area	30 m^2
applied inlet pressure	0.6 to 1.5 Mpa
Recovery rate	75%
Prefilter pore size	2 μm
Chemical agents	antiscalants (PW301N) biocides (NaOCl)
CIP chemical agents	NaOH, NaOCl, and citric acid

Stage 4	Value
Capacity	0.4 m^3/h
Activated carbon	coal-based granular
Contact time	40 min
Backwash	20 min every 7 days
Recovery rate	75%
DO	7.1~7.5 mg/L
Operation Condition	(a) Normal, (b) high TOC loading, (c) Low TOC loading

3. Results – Stage1 (Performance of Coagulation/Flocculation)

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Table 2. The average concentrations of major water quality indicators before and after the coagulation/flocculation unit.

Parameter	Influent	After Stage 1
pH	2.2	7.6
Conductivity	4,505	811
SS	4.1	4.0
VSS	0.7	0.8
TOC	5.8	4.9
COD_{cr}	63.7	14.1
T-N	13.1	12.3
NH_3-N	11.4	11.1
T-P	0.3	0.4
PO_4-P	0.1	0.0
F	542	12.2
[illegible]	[illegible]	[illegible]
Ca	[illegible]	122
Mg	0.06	6.87

① The effluent marked average F^- concentration of 12.2 mg/L-1, with removal rates greater than 98%

Parameter	Influent	After Stage 1
Na	15.6	11.5
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
Mn	0.008	0.161
W	25.8	9.9
Zn	0.209	0.018
T-Si	15.7	15.0
Ionic-Si	14.3	13.7
Acetaldehyde	0.947	0.136
Nitromethane	0.182	0.169
Methanol	0.846	1.023
Ethanol	1.678	0.872
Acetone	0.697	0.522
IPA	0.995	0.697
Acetonitrile	0.142	0.133

② More than 80% decrease in conductivity expected mitigation of inorganic fouling on the RO membrane

F^- removal mechanisms

▣ **Chemicals: $Ca(OH)_2$, PAC, Polymer**

- $Ca(OH)_2 + 2F^- + 2H^+ \rightarrow CaF_2 + 2H_2$
- $Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$
- $Al^{3+} + 6F^- \leftrightarrow AlF_6^{3+}$
- $AlF_6^{3+} + 3Na^+ \leftrightarrow Na_3AlF_6$

▶ $[Ca^{2+}]/[F^-]$ of 0.5 → F^- > 20~25 mg/L

▶ **$[Ca^{2+}]/[F^-]$ of 0.7** → F^- < 13 mg/L

Fig. 1. TOC removal under loading fluctuations

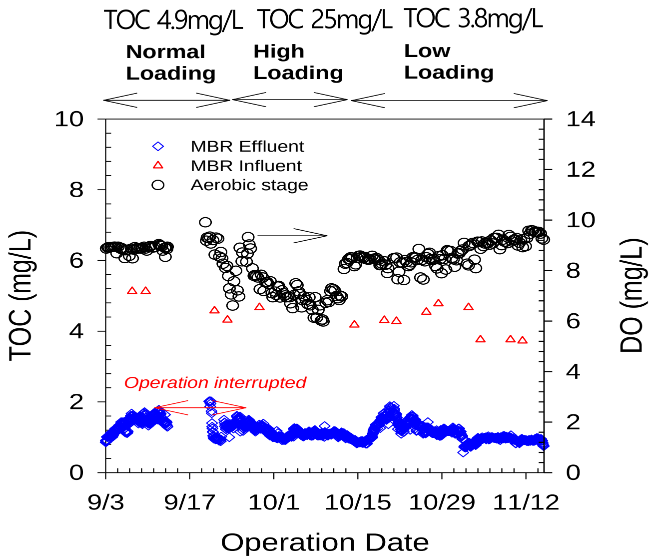


Table 2. GC/MS analysis on the primary organic constituents

Parameter	Normal loading		High loading		Low loading	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Acetaldehyde	0.321	<0.01	0.332	<0.01	0.112	<0.01
Nitromethane	0.155	0.026	0.141	<0.01	0.144	<0.01
Methanol	0.623	0.054	0.871	<0.01	0.748	0.033
Ethanol	1.41	0.011	2.57	<0.01	1.29	0.013
Acetone	0.397	<0.01	0.387	<0.01	0.485	<0.01
IPA	0.914	<0.01	0.726	<0.01	0.42	<0.01
Acetonitrile	0.107	0.01	0.101	<0.01	0.108	<0.01
Methylethylketone	0.01	<0.01	<0.01	<0.01	0.01	<0.01

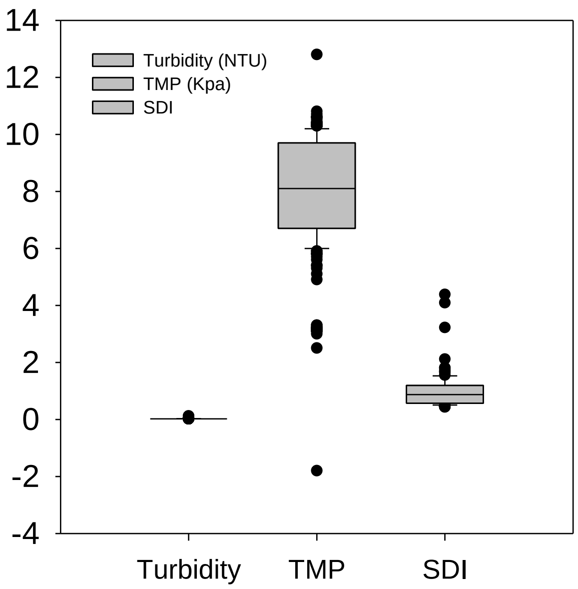
① Effluent TOC concentration was fairly stable throughout the whole operation

- Normal loading : 0.8 – 1.8 mg/L
- High TOC loading : 0.9 – 1.3 mg/L
- Low TOC loading : 0.6 – 1.3 mg/L

② GC/MS analysis on the effluent indicated that the primary organic constituents in the influent were almost perfectly transformed in the MBR regardless of the operational conditions

→ MBR were found to be appropriate pretreatment method to minimize the potential organic fouling in the following RO unit

Fig. 2. Turbidity, TMP, SDI_{15} during whole operation



① In spite of fluctuation in the SS concentration of stage 1 effluent between 1.2 and 6.6 mg L-1 (4.0 mg L-1 on average), the SS concentration of MBR effluent was always below detection limit.

② Permeate turbidity and SDI_{15} were consistently less than 0.03 NTU and 2.1, respectively to minimize the impact of suspended solids or colloidal particles on RO membrane fouling in stage 3

③ MBR unit could operate stably with flux at 20.7 LMH with relatively stable TMP near 9 kPa during the whole operation period.

- dTMP/dt was less than 0.5 kPa/d and, thus, the MC cycle was 1 month
- MC procedure with NaOCl (200 mg/L) followed by citric acid (2,000 mg/L)

3. Results – Stage3(Performance of Reverse Osmosis)

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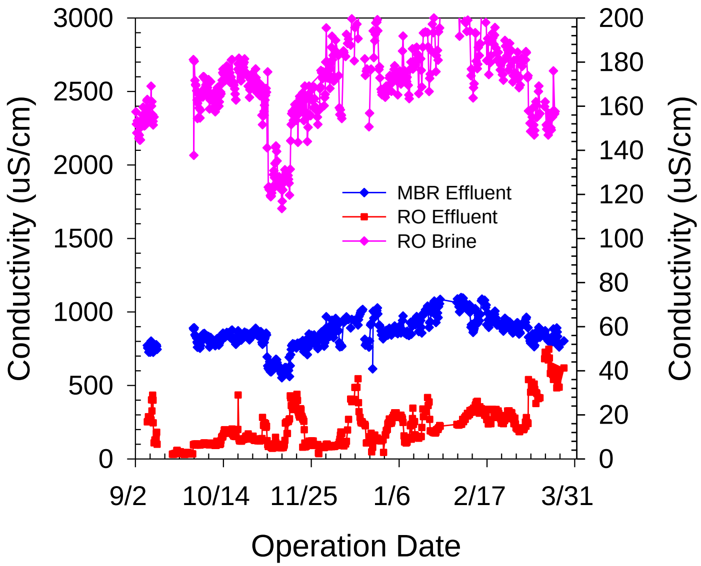
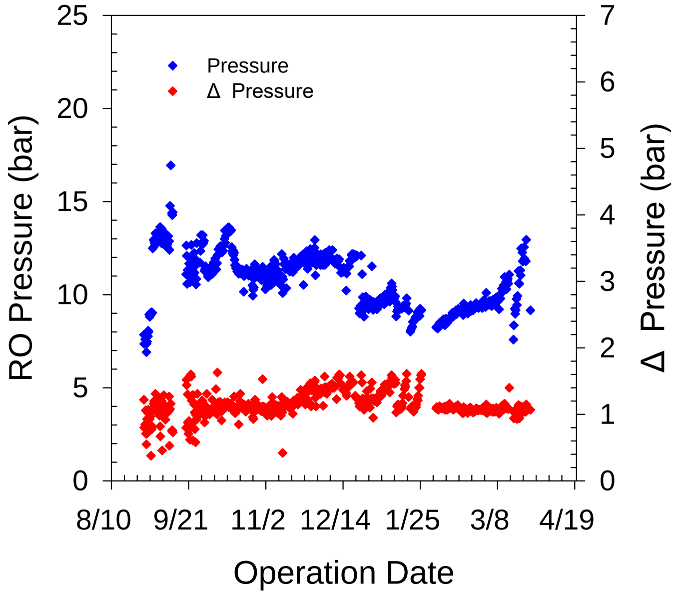


① Rejection of conductivity ranges 96.9 and 99.7% (99.4% on average)

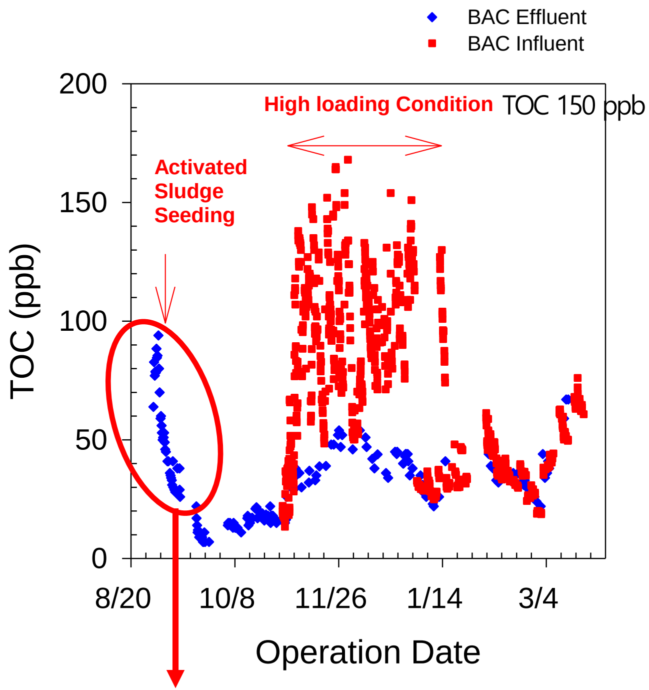
② TOC concentration in effluent below 34 ppb (17.6 ppb on average)

→ Effluent water quality actually met the criteria for feed water of UPW production facility.



① Permeate flux of 18 LMH with recovery of 75%

② TMP values reduced to the initial value (10 bar) by CIP cleaning with H_2SO_4 solution (pH = 1.5)



② Effluent TOC concentration was fairly stable throughout the whole operation

③ When TOC loading increased up to 150 ppb by addition of external carbon, effluent TOC concentration marginally increased up to 50 ppb, while the TOC removal efficiency was elevated to 60 - 78%.

→ Final BAC unit process could fully buffer a malfunction of stage 1 – 3 or a fluctuation in the pollutants loading of influent wastewater

① During this period, attached biofilm formation on the surface of activated carbon granules and acclimation could proceed.

Conclusion

1. In this work, the four-stage wastewater reuse system with coagulation/flocculation(CF), MBR, RO, and BAC unit process was evaluated to reuse a fluoride-rich inorganic semiconductor wastewater for the feed of ultrapure water production facility.
2. The combined CF and MBR were found to be appropriate pretreatment method to minimize the potential fouling in the following RO unit. Upon the pretreatment, the dominant foulants on the RO membrane surface were organic compounds which could be effectively removed by chemicals-in-place based on mixed sulfuric/citric acid.
3. While almost complete rejection of ionic species was observed in the RO unit, liquid chromatography with organic carbon detector revealed that more than 45% of the remaining total organic carbon (TOC) could be removed by the BAC treatment.
4. The TOC concentration in the final effluent was averaged to 0.35 ppb to satisfy the criteria to feed the UPW facility.
5. Our four-stage wastewater treatment system should be more competitive upon upcoming increases in public cost for water supply and wastewater treatment along with stricter environmental regulations.

Thank you
for Attention!!

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