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Sustainable Processes for Treatment of Waste Water Reverse Osmosis Concentrate to achieve Zero Waste Discharge: A Detailed Study in Water Reclamation Plant

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Abstract

Water reclamation systems based on dense membrane treatment such as reverse osmosis (RO) are being progressively applied to meet water quantity and quality requirements for a range of urban and environmental applications. The RO concentrate usually represents 25% of the feed water flow and contains the organic and inorganic contaminants at higher concentrations. The amount of RO concentrate waste water requiring disposal must be as minimal as possible (near zero-discharge); the recovery of high quality water should be as high as possible. Management issues related to proper treatment and disposal of RO concentrate are an important aspect of sustainable water reclamation practice. The RO concentrate is a significant component of water treatment process and poorly managed treatment and disposal of RO concentrate causes significant consequences. Even in a small to medium size water reclamation plant in Sydney, 2000 kL of water is treated by RO and around 300 kL of RO concentrate is produced daily. This RO concentrate consists of a high level of organics (25-30 mg/L of DOC which is mainly refractory organics) and inorganic salts ($\text{Cl}^- = 400\text{-}650$ mg/L, $\text{Na}^+ = 400\text{-}500$ mg/L, $\text{Ca}^{2+} = 93\text{-}200$ mg/L, $\text{K}^+ = 63\text{-}100$ mg/L). The RO concentrate waste disposal cost can be minimized and made valuable by reclaiming the RO concentrate with the aim of producing salts from the solutes and recycling the water to the treatment system. Technologies for recovery of high salt concentration from the RO concentrate such as forward osmosis (FO) and membrane distillation (MD) are either energy intensive or not developed in large scale. In this study, we highlight a sustainable membrane adsorption hybrid system in treating this RO concentrate.

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1.0 Introduction

Reverse osmosis concentrate (ROC) is the by-product of the reverse osmosis (RO) process that is rich in dissolved organics, persisting organic pollutants, inorganics, etc. The proper management and safe disposal of ROC is an important issue in water reclamation practices. Applying cost effective simple pre-treatments such as activated carbon adsorption and ion exchange resins prior to the discharge of ROC can serve as an alternative method for minimizing the entry of toxic constituents into the natural environment. Recently, the application of RO has grown as an alternative to conventional water treatment techniques due to its highly efficient removal capabilities. With the development of RO desalination, concern for potential environmental problems has grown. The production and discharge of a huge amount of concentrate is the major disadvantage of the RO process (Morillo J. et al, 2014). The RO concentrate produced in an RO plant as a by-product makes all the rejected contaminants by RO and comprised of concentrated stream 4-7 times larger than RO feed (Wang, W, et al, 2013). The improper discharge of such reverse osmosis concentrate (ROC) may potentially cause human and ecological health problems because this may contain high concentrations of rejected compounds such as refractory substances and pharmaceuticals and personal care products (PPCPs). The discharge of RO concentrate in large quantities causes a considerable loss of water resources and damages the environment (Ge J, Peng Yet al 2014). As such, providing a ROC treatment prior to discharge is mandatory to ensure any potential health hazards to the environment and living creatures are circumvented (Radjenovic J. Et al, 2011; Pérez-González Urtiaga et al, 2012).

For example an RO-based advanced water reclamation plant was planned for construction in Canberra, Australia in 2007. However, the sustainable management of ROC remains a major environmental and economic hurdle for the plant and has limited the implementation of the membrane processes (Umar M, et al 2013). In Queensland, Australia, the Bundamba advanced wastewater treatment plant which is part of Australia's largest water recycling scheme is required to treat its ROC and monitor the nutrients and metal concentration in the effluent prior to its discharge into Brisbane River (Vargas C, et al, 2011). The installation of proper systems for the treatment and management of ROC produced from inland water treatment plants is mandatory in order to safeguard the ecology of receiving water bodies.

Concentrate disposal is normally considered to be a major issue in the engineering design of any desalination facility (Ahmed M, et al, 2001). For a typical brackish water desalination plant, the cost of brine disposal incurs an additional 15% of the total cost of desalination for an inland desalination compared to plants disposing brine into the sea (Glueckstern P, et al, 1997).

In this study, we have evaluated the performance of microfiltration-granular activated carbon (MF-GAC) adsorption hybrid system in treating ROC. This was assessed in terms of transmembrane pressure (TMP) development and dissolved organic carbon (DOC) removal. Further, detailed analysis on the removal of organics and pharmaceuticals and personal care products (PPCPs) was carried out to investigate the efficiency of this process in removing these contaminants from ROC.

2.0 Materials and methods

2.1 Reverse Osmosis Concentrate (ROC)

The ROC samples collected from a full scale Microfiltration/reverse osmosis (MF/RO) water reclamation plant located in Sydney, Australia were used as feed water. The plant treats a combination of storm water and biologically treated sewage effluent. This plant produces around 300 kL of ROC/day and is discharged directly into a sewer system (Chapman H, 2006). The detailed characteristics of ROC used in this study are summarised in Table 1.

Table 1: Physico-chemical characteristics of ROC

Characteristics	Value	
Conductivity ($\mu\text{S}/\text{cm}$)	2350	
pH	7.5	
DOC (mg/L)	25-30	
TDS (mg/L)	2250	
Anions (mg/L)	Fluoride	3.0 – 4.0
	Chloride	400 – 650
	Nitrite	1.3 -1.5
	Bromide	1.0 – 1.5
	Nitrate	23– 26
	Phosphate	8– 9
	Sulfate	220 – 250
Cations(mg/l)	Na	400–500
	K	63-100
	Ca	93-200
	Mg	65 – 72

2.2 Membrane

Hollow fibre membrane made of hydrophilic modified polyacrylonitrile (PAN) (MANN+HUMMEL ULTRA-FLO PTE LTD, Singapore) was selected for use in the long term MF-GAC hybrid system. The surface area of this membrane was 0.1 m^2 with a membrane nominal pore size of $0.1 \mu\text{m}$. The inner and outer diameters of the hollow fibres were 1.1 and 2.1 mm, respectively.

2.3 Adsorbent

Coal-based premium grade GAC (MDW4050CB) was supplied by James Cumming & Sons Pty Ltd. Australia and used as an adsorbent. The detailed characteristics of GAC are given in Table 2.

Table 2: Characteristics of GAC

Item	Characteristics / Value
Type/structure	Coal-based premium grade (MDW4050CB)
Exchange/adsorption Capacity	Iodine #1000mg/g
Moisture content	2% max
Particle size	425-600 μm
Surface area	1000 \pm 50 sqm/g
Adsorption average pore diameter	30 \AA

2.4 Microfiltration-granular activated carbon hybrid system

The schematic diagram of MF-GAC hybrid system is depicted in Figure 1. A hollow fibre membrane module was immersed in a 3 L influent tank containing the ROC to be treated. The membrane reactor tank was continuously fed with ROC at a constant rate. Both inflow and outflow were maintained at constant rates by peristaltic pump. Air flow was provided at a rate of $1.5 \text{ m}^3/\text{m}^2$ membrane area.h to produce scouring on the membrane surface as well as to keep the GAC particles in suspension in the reactor.

Long term experiment was conducted with an initial GAC dose of 10 g/L (volume of the reactor) which was predetermined based on adsorption isotherm results (not presented here). Following this, 10% of GAC of initial concentration in the reactor was replaced with new GAC on a daily basis to maintain good removals of DOC. The hydraulic residence time was 6.7 h (~ 410 mins).

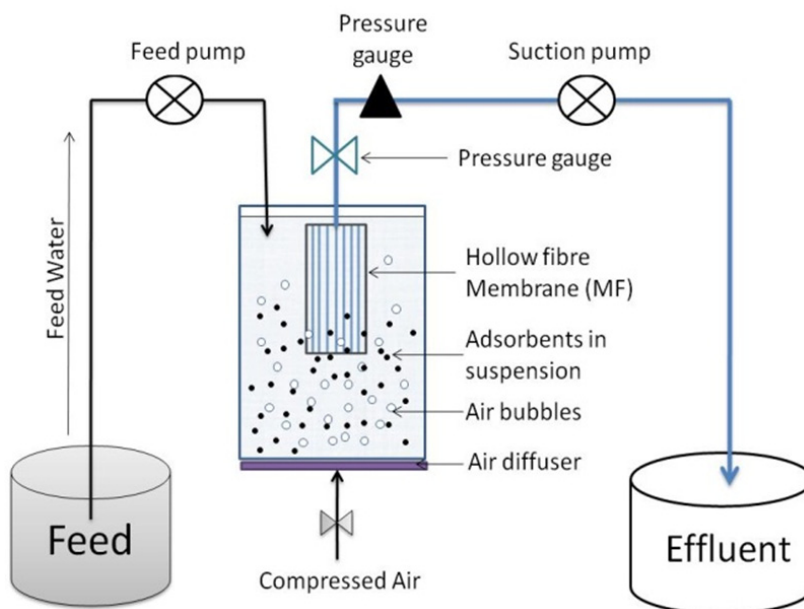


Fig.1. Schematic diagram of the submerged MF-GAC hybrid system

Effluent samples were collected daily for the measurement of effluent DOC. Samples collected on day 1 and day 7 were also used for the measurement of PPCPs concentrations. The analyses were done in triplicate both for bulk feed water and effluent water. From this an average concentrations of PPCPs for influent as well as effluents were measured. The TMP was continuously monitored using an online pressure transducer and data logger equipped with digital monitor. The data was then downloaded from the data logger in the computer for the calculation of TMP development.

2.5 Analytical methods

The DOC was measured after filtering through a 0.45 μm filter using a Multi N/C 2000 analyser (Analytik Jena AG). Pharmaceuticals and personal care products (PPCPs) were extracted using solid phase extraction (SPE) and examined employing Liquid Chromatograph with tandem mass spectroscopy. 5 mL analytes were extracted using 500 mg hydrophilic/lipophilic balance (HLB) cartridges (Waters, Milford, MA, USA). These analytes were separated using an Agilent (Palo Alto, CA, USA) 1200 series high performance liquid chromatography (HPLC) system equipped with a 150 x 4.6 mm, 5 μm particle size, Luna C18 (2) column (Phenomenex, Torrance, CA, USA). Mass spectrometry was done using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with a turbo-V ion source employed in both positive and negative electro-spray modes. All calibration curves had a correlation coefficient of 0.99 or better.

The analysis of inorganic anions was done using a Metrohm ion chromatograph (Model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. Separation was achieved using an A SUPP column 3 (4-150 mm). Solutions of Na_2CO_3 (3.2 mmol/L) and NaHCO_3 (1.0 mmol/L) were used as mobile phase with a flow rate of 0.7 mL/min. The concentrations of inorganic cations were carried out using 4100 MP-AES (Microwave Plasma-Atomic Emission Spectrometry).

3.1 Results and discussion

3.2 DOC and TMP development

The ten days long MF-GAC treatment was observed to be effective in removing DOC from ROC. The initial dose of 10 g/L GAC was applied into the reactor to reduce the direct organic load onto the membrane surface by adsorption of the DOC onto GAC so that the TMP development can be reduced. Thus, the removal of DOC was maintained at 50-80% whilst the TMP was observed to increase from 10 kPa to 60 kPa over the 10 days (Figure 2). The amount of ROC treated per day by 10% of GAC was 10.5 L. This corresponds to a GAC dose of 0.285 g per litre of ROC treated. The system is capable of maintaining more than 50% DOC removal from 105 L of RO concentrate using a total of 40 g of GAC for 10 days.

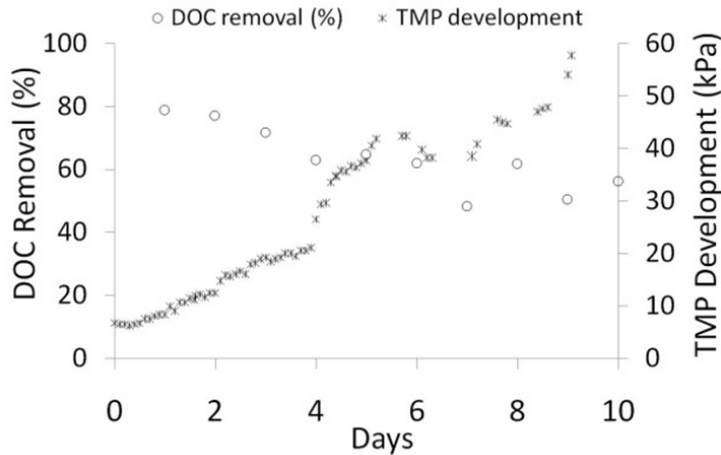


Fig. 2. DOC removal efficiency and TMP development of the long-term submerged MF-GAC hybrid system used in treating ROC (Flux = 10 L/m²/h; Initial GAC dose = 10 g/L; 10% GAC daily replacement).

3.3. Removal of pharmaceuticals and personal care products (PPCPs)

The 10 days long MF-GAC removed overall 60% to more than 99% of organic micro pollutants from ROC in which the removals were noticed to be higher at day 7 than day 1 (Table 3). Conversely a decreasing trend of DOC removal was observed in which the removals at day 1 (78%) was higher than that at day 7 (50-60%). The marked increase in micro pollutants removal with time despite a small decrease in DOC removal shows that the adsorption of micro pollutants was not significantly affected by the presence of DOC in ROC. The reason for this phenomenon can be explained as follows: The molecular weights (MWs) of micro pollutants are much smaller than the MWs of natural organics as such the access to the fine pores of GAC by micro pollutants is faster than the bulky natural organics. Furthermore, the 10% daily GAC replacement provides new binding sites in which more incoming micro pollutants can be adsorbed quickly onto GAC than natural organics and this resulted to increased removal of organic micro pollutants. Thus, the 10% GAC daily replacement helped to minimize pore blockage and competitive effect of natural organics for GAC binding sites and maintained the removal of micro pollutants well throughout the experiment.

Table 3: The removal of organic micro pollutants by MF-GAC hybrid system from ROC

Organic Micro Pollutants	Submerged MF-GAC hybrid system				
	Influent (ng/L)	Effluent (ng/L)		Removal (%)	
		Day 1	Day 7	Day 1	Day 7
Amtriptyline	45	<5	<5	>89	>89
Atenolol	466	<5	<5	>99	>99
Caffeine	1410	31	<5	98	>99
Carbamazepine	2240	86	<5	96	>99
Clozapine	68	<5	<5	>93	>93
DEET	68	27	<5	60	>93
Diclofenac	337	<5	<5	>99	>99
Fluoxetine	47	<5	<5	>89	>89
Gemfibrozil	344	9	<5	97	>99
Ketoprofen	377	<5	<5	>99	>99
Naproxen	443	10	<5	98	>99
Paracetamol	114	<5	<5	>96	>96
primidone	26	<5	<5	>81	>81
Simazine	80	<5	<5	>94	>94
Sulfamethoxazole	144	35	<5	76	>97
Triclocarban	162	<10	<10	>94	>94
Triclosan	211	<5	<5	>98	>98
Trimethoprim	974	9	<5	99	>99
Verapamil	83	<5	<5	>94	>94

The micro pollutants removal data obtained for day 1 only was considered to explain the removal mechanisms as the concentrations of all the micro pollutants removed at day 7 were less than the detection limit of 5 – 10 ng/L. As the degree of the removal of micro pollutants is influenced by the combination of solute Log K_{ow} and pKa values, the Log K_{ow} values were corrected and the corrected value is expressed as Log D values¹¹.

The plot of removal (%) of micro pollutants vs the calculated Log D values is illustrated in Figure 3 where micro pollutants having higher Log D values are noticed to be highly removed by GAC (de Ridder DJ. Et al, 2009). In addition, positively charged were efficiently removed by GAC than negative solutes on pre-loaded carbon for example, negatively charged pollutants such as sulfamethoxazole and DEET showed less removals (upto 66 – 70%) compared to the rest whilst all the positively charged pollutants have achieved removals up to 98 – 100%. This can also be due to charge interactions in which a GAC particle loaded with organics may carry negative charges which has the tendency to attract positively charged pollutants and may repel negatively charged compounds. This fact can be supported by the 99% removal of positively charged trimethoprim (Log K_{ow} 0.91; pKa 7.1) and could be explained based on attractive forces towards GAC rather than based on Log D values. This is in agreement with de Ridder et al. (2009)¹¹ who stated positively charged solutes were removed 20-40% more than that of negatively charged compounds due to charge interactions.

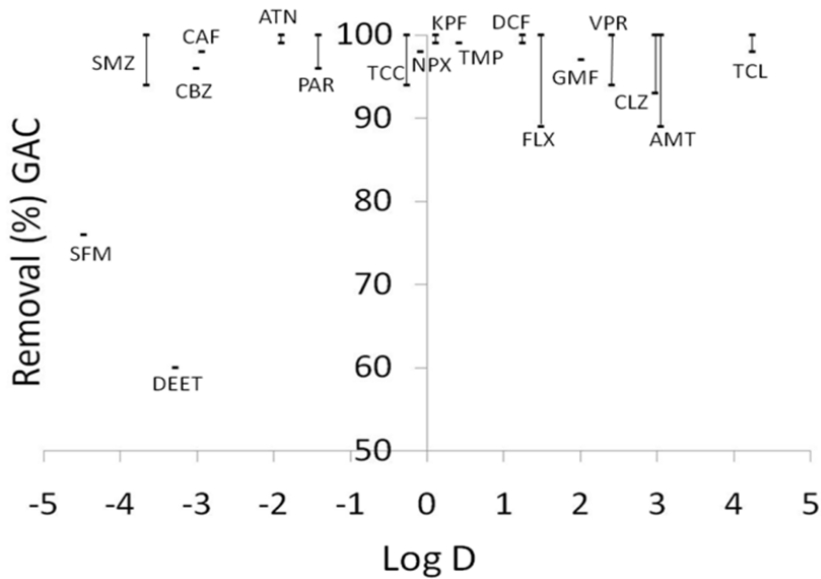


Fig. 3. Removal of organic micro pollutants by MF/GAC hybrid system from ROC as the

function of calculated Log D [CAF – Caffeine; ATN – Atenolol; TMP – Trimethoprim; PAR – Paracetamol; SMZ – Simazine; SFM – Sulfamethoxazole; CBZ – Carbamazepine; KPF – Ketoprofen; NPX – Naproxen; CLZ – Clozapine; VPR – Verapamil; FLX – Fluoxetine; DCF – Diclofenac; GMF – Gemfibrozil; TCL – Triclosan; TCC – Trichlorocarbon; AMT – Amitriptyline; DEET - Diethyltoluamide]

3.4 Advantage of long term operation of MF-GAC hybrid system

MF-GAC hybrid system was found to be more efficient in removing DOC and organic micro pollutants over the experimental duration at 10 g/L initial dose of GAC and followed by 10 % daily GAC replacement. With time, the removal of micro pollutants was observed to be increasing whilst the removal of DOC decreased. At the end of day 1, MF-GAC removed 63% of total number of organic micro pollutants below the detection limit of 5 – 10 ng/L in the treated effluent. In the long-run (day 7 sample), excellent removals of micro pollutants using MF-GAC were observed where all the pollutant concentrations in the treated water were less than the detection limit of 5 – 10 ng/L. According to past studies, the presence of organics in the feed water reduces the removal of micro pollutants by competing for GAC binding sites and pore blocking, however, on contrary, the removal of micro pollutants was noticed to be increasing with time in this study. The higher removals of micro pollutants observed at later stage by MF-GAC hybrid system than at beginning of the experiment can be explained based on charge interactions, less competitive effects etc. as follows.

As the ROC contained plenty of negatively charged organics (20 – 30 mg/L), the GAC particles suspended in the reactor may get easily preloaded with DOC. The preloaded GAC carries negative charges which can easily attract positively charged micro pollutants¹¹. Besides this factor, the introduction of new GAC brings more unoccupied binding sites which may preferentially adsorb more incoming micro pollutants than DOC as micro pollutants are smaller molecules than DOC thus the access to the fine pores of GAC by micro pollutants is faster than the DOC.

This MF/GAC system is also considered as cost effective in micro pollutants removals compared to nanofiltration or reverse osmosis processes. Based on a cost analysis study, MF or ultrafiltration (UF) combined with PAC system was found to be cheaper than the integration of NF systems which is not competitive as long as the removal of inorganic ions are not required (Pianta R et al, 2000). The treatment cost (including capital and O&M cost) of UF/PAC was ~ 35 c Euro/m³ whilst the treatment cost of UF/NF system was ~ 55 c Euro/m³ for a plant size of 30 m³/h¹². There is no significant cost difference between MF and UF. In our study, the MF/GAC hybrid system

was conducted with a filtration flux of 10 L/m².h with the applied pressure of 27-85 kPa. As per our preliminary NF studies (NF membrane: NTR 729HF) the estimated applied pressure was 100 kPa to achieve similar flux 10 L/m².h with ROC. In addition, the removal of micro pollutants by the NF was observed to be declining with time due to membrane saturation. Further, the management of NF/RO concentrate is another issue of NF/RO processes that needs further treatments with added costs. These limitations of NF/RO membranes favour the application of MF/GAC hybrid system in terms of the removal of micro pollutants from ROC prior to discharge into environment.

4.0 Conclusion

Long term MF-GAC operated for 10 days was observed to be effective in terms of removals of dissolved organics and organic micro pollutants. The daily GAC replacement of 10% of total GAC i.e., 0.28 g of GAC/L treated water per day maintained DOC and micro pollutants removals more than 50% and more than 60% from ROC over 10 days. Further, competitive effect of organic micro pollutants with dissolved organics for GAC binding sites also was minimized at this higher dose. Thus, MF-GAC is a cost effective system in removing DOC and micro pollutants from ROC compared to NF/RO membrane processes in terms of cost and energy, removal efficiencies, concentrate management etc. This system can be installed at WWTP to treat the ROC either prior to discharge into environment or using as feed to RO.

Finally, MF-GAC is an effective system for treating ROC to remove dissolved natural and persisting organics prior to discharge into the environment in a safe manner. Alternatively the effluent can be recirculated and mixed with other feed to a RO process to maximise water reuse.

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References

- 1) Ahmed M, Arakel A, Hoey D, Coleman M (2001) Integrated power, water and salt generation: a discussion paper. *Desalination* 134:37-45.
- 2) Chapman H (2006) WRAMS, sustainable water recycling. *Desalination* 188 (1-3):105-111.
- 3) de Ridder DJ, McConville M, Verliefe ARD, van der Aa LTJ, Heijman SGJ, Verberk JQJC, Rietveld LC, van Dijk JC (2009) Development of a predictive model to determine micropollutant removal using granular activated carbon, *Drinking Water Engineering Science Discuss* 2(2): 189-204.
- 4) Glueckstern P, Priel M (1997) Optimized brackish water desalination plants with minimum impact on the environment. *Desalination* 108:19-26.
- 5) Ge J, Peng Y, Li Z, Chen P, Wang S (2014) Membrane fouling and wetting in a DCMD process for RO brine concentration. *Desalination* 344: 97-107.
- 6) Morillo J, Usero J, Rosado D, El Bakouri H, Riaza A, Bernaldo FJ (2014) Comparative study of brine management technologies for desalination plants. *Desalination*, 336: 32-49.
- 7) Pérez-González Urriaga, AM, Ibáñez R, Ortiz I (2012) State of the art and review on the treatment technologies of water reverse osmosis concentrates. *Water Res* 46:267-283.
- 8) Pianta R, Boller M, Urfer D, Chappaz A, Gmünder A (2000) Costs of conventional vs. membrane treatment for karstic spring water. *Desalination* 131:245-255.
- 9) Radjenovic J, Bagastyo A, Rozendal RA, Mu Y, Keller J, Rabaey K (2011) Electrochemical oxidation of trace organic contaminants in reverse osmosis concentrate using RuO₂/IrO₂-coated titanium anodes. *Water Res* 45: 1579-1586.
- 10) Umar M, Roddick F, Fan L (2013) Recent advancements in the treatment of municipal wastewater reverse osmosis concentrate-An overview. *Crit Rev EnvSciTechnol* 45(3):193-248
- 11) Vargas C, Buchanan A (2011) Monitoring Ecotoxicity and Nutrients Load in the Reverse Osmosis Concentrate from Bundamba Advanced Water Treatment Plant, Queensland Australia. *Water Prac Tech* 6(1):doi:10.2166/wpt.2011.006
- 12) Wang, W, Gu, P, Zhang, G, Wang L (2013) Organics removal from ROC by PAC accumulative countercurrent two-stage adsorption-MF hybrid process - A laboratory-scale study. *Sep PurifTechnol* 118: 342-349.