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**Declarations of interest: none**

**Removal of organic matter from wastewater reverse osmosis concentrate using granular activated carbon and anion exchange resin adsorbent columns in sequence**

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**Abstract:** Reverse osmosis concentrate (ROC) generated as a waste stream during reverse osmosis treatment of reclaimed wastewater, presents significant disposal challenges. This is because it causes environmental pollution when it is disposed to lands and natural water bodies. A long-term dynamic adsorption experiment was conducted by passing ROC from a wastewater reclamation plant, firstly through a granular activated carbon (GAC) column, and subsequently through an anion exchange resin (Purolite) column, for the removal of two major ROC pollutants, namely dissolved organic carbon (DOC) and microorganic pollutants (MOP). GAC removed most of the smaller-sized low molecular weight neutrals and building

block fractions as well as the hydrophobic fraction of DOC with much less removal by the subsequent Purolite column. In contrast, the humics fraction was less well removed by the GAC column; however, Purolite column removed all that was remaining of this fraction. This study demonstrated that combining adsorbents having different affinities towards a variety of DOC fractions constitute an effective method of taking advantage of their different properties and achieving larger DOC removals. Almost 100% of all 17 MOPs were removed by the GAC column, even after 2880 bed volumes of continuous use. This contrasted with the DOC fractions' removal which was much lower.

**Keywords:** dissolved organic carbon, reverse osmosis concentrate, anion exchange resin, granular activated carbon

### **Highlights**

- Combined GAC + anion exchange resin columns removed all DOC fractions of ROC.
- GAC removed all 17 microorganic pollutants at 2880 BV of use but not DOC.
- GAC had higher affinity for smaller-sized DOC fractions and hydrophobic fraction.
- Anion exchange resin (Purolite) had higher affinity for humics fraction of DOC.

## **1. Introduction**

Reverse osmosis concentrate (ROC) is a concentrated waste stream produced by the RO process during wastewater reclamation. The high-quality water produced by this commonly practiced process (70-75% of the wastewater volume) can be used as potable and non-potable recycled water. However, the ROC waste generated in this process is a serious problem because it can cause environmental pollution when it is disposed to lands and natural

water bodies (Roberts et al., 2010). This is due to the presence of many pollutants contained in ROC at concentrations approximately three to four times those in the wastewater (Jamil et al., 2018). These pollutants need to be removed before ROC can be safely disposed of. The two major groups of pollutants in ROC are organic matter (OM) and micro-organic pollutants (MOP), the latter include pharmaceutical and personal care products, endocrine disruptors, pesticides, and industrial by-products (Arola et al., 2019; Shanmuganathan et al., 2017; Wang et al., 2013; Zhou et al., 2011). At high concentrations, OM can cause colour, taste and odour problems and reduce the effectiveness of the water treatment process (Bolto and Gregory, 2007; Korotta-Gamage and Sathasivan, 2017; Matilainen et al., 2010; Mohiuddin et al., 2014). On the other hand, many MOPs are known to be toxic to freshwater invertebrates (such as daphniids), fish, mussels, and human embryonic cells even at very low concentrations (Pal et al., 2010).

Number of advanced treatment options have been suggested for the removal of these persistent organics in wastewater, such as chemical oxidation, activated carbon (AC) adsorption, and membrane filtration. Chemical oxidation using ozone, alone or in combination with additional physical/chemical agents (i.e., advanced oxidation), has proved a highly effective treatment for a wide spectrum of emerging aqueous organic pollutants, including pesticides, pharmaceuticals, personal care products, and endocrine disruptors in surface water and wastewater (Ikehata et al., 2008, Snyder et al., 2006; Wang and Wang, 2016; Zhou et al., 2011). Granular and powdered AC (GAC and PAC) have been successfully tested in adsorption columns and membrane hybrid systems, and extended to pilot- and full-scale treatment systems to remove DOC and MOPs found in wastewater (Delgado et al., 2012; Kennedy et al., 2015; Li et al., 2011; Snyder et al., 2007; Ye et al., 2019). Nanofiltration (NF) in combination with an upstream PAC treatment was successfully tested for high quality water reuse of tertiary effluent from a municipal wastewater treatment plant. The PAC/NF process provided a consistently high permeate quality with respect to bulk

and trace organics (Kazner et al., 2008). In this study, adsorption is used to remove DOC and MOPs because of its simplicity and minimum waste generation (Cooney, 1999). AC adsorption has proved effective in removing trace organic contaminants due to the very high surface area of AC and the combination of its well-developed pore structure and surface chemical properties, and because transformation products are not generated during the process (Delgado et al., 2012).

DOC and MOPs are composed of chemical compounds with different characteristics varying in molecular weight, electrical charge, hydrophobicity/hydrophilicity, and functional groups, such as hydrophobic dissolved organic carbon (DOC) and hydrophilic DOC (humics, low molecular weight (LMW) neutrals, building blocks, biopolymers) (Delgado et al., 2012; Huber et al., 2011; Jamil et al., 2019a; Velten et al., 2011; Wang et al., 2013). Therefore, the adsorbent must have surface characteristics that can effectively remove much of these different types of DOC and MOP compounds. Yet, this is difficult to achieve to a satisfactory degree using a single adsorbent, because each adsorbent has a specific surface physico-chemical characteristic dominance which is capable of removing an adsorbate having only a compatible range of attributes (Cornelissen et al., 2008; Shanmuganathan et al., 2014). Of the different adsorbents, AC and anion exchange resins are popular and have some differences in surface characteristics which complement each other in targeting the diverse attributes of DOC and MOPs. Activated carbon, which is a traditional and versatile adsorbent, has been effectively used to remove several pollutants including DOC and MOPs. Several review articles have documented numerous research studies on the use of AC in removing MOPs in water and wastewater, and concluded that AC is a promising adsorbent that can be used to effectively reduce the concentrations of MOPs (Delgado et al., 2012; Jeirani et al., 2017; Wang and Wang 2016). The mechanisms of adsorption were summarised to include hydrophobicity,  $\pi$ - $\pi$  bonding by electron donor-accepter complexation, H-bonding, and electrostatic interaction, between the AC and the MOPs. Activated carbon has also been used

for many decades to remove DOC. The high adsorption capacity of AC towards DOC has been linked to its well-developed internal pore structure, high surface area and the presence of a wide spectrum of surface functional groups (Chingombe et al., 2005; Hatt et al., 2013; Summers and Roberts, 1988; Velten et al., 2011). Anion exchange resins have also been successfully used to remove DOC from water (Bolto et al., 2004; Chingombe et al., 2005). The main mechanism of adsorption here is exchange of anionic species of DOC (humic acid) with the chloride ions in the resins (Cornelissen et al., 2008). Bolto et al. (2004) reported that anion exchange resin removal of charged species of DOC was more efficient than neutral molecules. Influence of resin properties such as charge density, the number of secondary amine groups, structure (cross-links vs open structure) and degree of basicity determine the effectiveness of the resin in removing DOC.

Though there are many studies on AC and anion exchange resins used separately, information on their combined use in removing DOC or MOP is limited. Humbert et al. (2008) reported that simultaneous and successive combinations of anion exchange resins and an AC significantly improved the removal of two pesticides from water compared with AC treatment alone in a batch adsorption study. The improved removal of the pesticides was explained as due to adsorption of high molecular weight DOC species by the anion exchange resins which reduced the AC pore blockage phenomena. In another study, Hu et al. (2014) stated that during short-term (< 350 bed volumes) fixed-bed AC adsorbent filtration, raw water pre-treated with an anion exchange resin (Lewatit VP OC 1071) slightly prolonged the breakthrough of the investigated MOPs (atrazine, caffeine) compared to the breakthrough during filtration of untreated water. This was attributed to the smaller amount of pore blockage that occurred with a lower content of 'humic substances' and 'building blocks' in the pre-treated water.

Our previous study showed that a GAC and an anion exchange resin (Purolite), because of their contrasting charge, hydrophobicity, and porosity characteristics, had different

abilities to adsorb the different DOC fractions and by combining these two adsorbents, one after the other, most of the DOC fractions could be successfully removed (Jamil et al., 2019b). However, this study, like the other studies reported before, was conducted in static short-term laboratory batch experiments, the results of which cannot be directly applied to the dynamic fixed-bed adsorption conditions used in actual water treatment plants.

This paper presents the results of a study conducted using two previously tested adsorbents (Jamil et al., 2019b), but in a dynamic long-term column experiment, the results of which can be scaled-up to actual water treatment plants. The aims of the research were to: firstly, determine the breakthrough characteristics of DOC and its fractions in ROC through a GAC column followed by a Purolite A502PS anion exchange column arranged in a sequential order; secondly, determine the percentage removal of the DOC fractions by the two columns at various times; thirdly, determine the percentage of 17 MOPs removal from ROC. The novelty of this study is the use of an anion exchange resin and GAC in separate columns arranged in sequence to investigate the removal of all DOC fractions and 17 MOPs in each column over a long period (2880 bed volumes). The study was conducted for a long duration to understand the validity of this process for sustainable operation. Previous studies on combination of adsorbents were conducted in batch adsorption system or short-term column experiments, and not always on both DOC fractions and large number of MOPs.

## **2. Materials and methods**

### *2.1. ROC characteristics*

The ROC used in these experiments originated from the Sydney Olympic Park water reclamation plant. Stormwater and biologically treated sewage effluents are treated in this plant. The plant produces approximately 72% of clean water and 28% ROC. The characteristics of the ROC used are presented in Table 1. Between the hydrophilic fraction

and hydrophobic fraction, the former is predominant and amounts to 72%. Of the hydrophilic fractions, the humics fraction had the highest percentage (50%). A higher percentage of hydrophilic fraction than hydrophobic fraction, and humics being the main component of the hydrophilic fraction, were also reported for other ROC samples (Jamil et al., 2019a,b; Shanmuganathan et al. 2015), wastewater (Shanmuganathan et al., 2014), and lake waters (Velten et al., 2011). The concentrations of MOPs (ng/L) were much lower than those of DOC fractions (mg/L) and they had a wide variation (31-8180 ng/L) (Table 2).



**Table 1.** ROC characteristics

Parameter	Unit	Value
pH		7.78
Conductivity	mS/cm	2.68
Mg <sup>+2</sup>	mg/L	60.6
Ca <sup>+2</sup>	mg/L	98.5
K <sup>+</sup>	mg/L	75.9
Na <sup>+</sup>	mg/L	432
Silica as Si	mg/L	7.43
PO <sub>4</sub> <sup>-3</sup>	mg/L	3.16
SO <sub>4</sub> <sup>-2</sup>	mg/L	279
NO <sub>3</sub> <sup>-</sup>	mg/L	32.2
Cl <sup>-</sup>	mg/L	543
Total DOC	mg/L	45.8
Hydrophobic DOC	mg/L	12.8
Hydrophilic DOC	mg/L	32.9
Biopolymers in DOC	mg/L	1.4
Humics in DOC	mg/L	16.7
Building blocks in DOC	mg/L	5.0
LMW neutrals in DOC	mg/L	9.6

**Table 2.** Concentrations of MOPs in ROC before (feed solution) and after (effluent) 9.5 days (2880 bed volumes) treatment with GAC column.

MOP	MOP Class	Limit of quantification(ng/L)	Charge	Log Kow* pH7	Before treatment (ng/L)	After treatment (ng/L)	% removal
Atrazine	Herbicide	5	0 <sup>a</sup>	2.61 <sup>a,f</sup>	31	0	100
Benzotriazole	Drug precursor	5	0 <sup>b</sup>	1.44	8180	20	100
Caffeine	Stimulant	5	0 <sup>b,c,d</sup>	-0.07 <sup>g</sup>	1104	16	99
Carbamazepine	Antiepileptic	5	0 <sup>b,c</sup>	2.45 <sup>h,g</sup>	1010	0	100
Diclofenac	Analgesics	5	- <sup>b,c</sup>	4.5- 4.8 <sup>i,g</sup>	594	0	100
Diuron	Herbicide	5	0 <sup>b</sup>	3.49 <sup>b</sup>	924	0	100
Gemfibrozil	Lipid regulator	5	- <sup>b,c</sup>	4.7 <sup>k</sup>	698	0	100
Ibuprofen	Analgesic	5	- <sup>b,d</sup>	3.5- 4.5 <sup>i,g</sup>	538	0	100
Ketoprofen	Relieve pain	5	- <sup>c,d</sup>	3.12 <sup>c</sup>	74	0	100
Naproxen	Analgesics	5	- <sup>c,d</sup>	3.2 <sup>i,c,f</sup>	920	0	100
Paracetamol	Pain reliever	5	0 <sup>b,c,d</sup>	0.46 <sup>c</sup>	67	0	100
Saccharin	Artificial sweetener	50	0 <sup>b</sup>	0.91 <sup>e</sup>	4260	0	100
Simazine	Herbicide	5	0 <sup>c,e</sup>	2.18 <sup>c,e</sup>	31	0	100
Sulfamethoxazole	Antibiotic	5	- <sup>b,c</sup> ; 0 <sup>d</sup>	0.89 <sup>f,k</sup>	566	29	95
TCEP	Reducing agent	5	0 <sup>e</sup>	1.44 <sup>k</sup>	836	19	98
Triclocarban	Antibacterial agent	10	0 <sup>c,e</sup>	4.9 <sup>l</sup>	60	0	100
Trimethoprim	Antibiotic	5	0 <sup>b,c,d</sup>	0.91 <sup>g,m</sup>	600	0	100

\*Kow represent octanol-water partition coefficient of the MOPs.

<sup>a</sup><https://pubchem.ncbi.nlm.nih.gov/compound/benzophenone>; <sup>b</sup>Calculated with Advanced Chemistry Development (ACD/Labs) Software V9.04 for Solaris; <sup>c</sup>Shanmuganathan et al. (2017);

<sup>d</sup>Hajibabania et al. (2011); <sup>f</sup>Yangali-Quintanilla et al. (2009); <sup>g</sup>Yang et al. (2011); <sup>h</sup>Ternes and

Joss (2006); <sup>i</sup>Serrano et al. (2011); <sup>k</sup>Westerhoff et al. (2005); <sup>l</sup>Loftsson et al. (2005); <sup>m</sup>U.S. National Library of Medicine (<http://chem.sis.nlm.nih.gov/chemidplus/rn/52-53-9>).

## 2.2. Adsorbent characteristics

A coal based GAC (MDW/4050CB) obtained from James Cumming and Sons Pty Ltd. Australia and Purolite A502PS obtained from Purolite Corporation, USA were used for the study. The particle size of GAC was 0.42-1.68 mm (majority 0.42-0.60 mm and 95% less than 1.00 mm) and that of Purolite was 0.43-0.60 mm (Shanmuganathan et al., 2014). The BET surface areas ( $\text{m}^2/\text{g}$ ) of the two adsorbents were 1000 and 21, respectively. The GAC had a pore volume and average pore diameter of  $0.69 \text{ cm}^3/\text{g}$  and 2.7 nm, respectively (Eeshwarasinghe et al., 2018). The Purolite structure consists of polystyrene cross-linked with divinylbenzene. The functional groups of Purolite are quaternary ammonium ion whose positive charge is balanced by negatively charged chloride ions

## 2.3. DOC and MOP analyses

The DOC fractionation was performed using a liquid chromatography-organic carbon and nitrogen detector (LC-OCD) system model 8, based on the Grantzel thin film reactor developed by DOC Labor, Dr. Huber, Germany. The LC-OCD is an automated size-exclusion chromatography system coupled to three detectors, for organic carbon, organic nitrogen and UV absorbance analysis. The measurement procedure has been described in full by Huber et al. (2011). LC-OCD separates the sample into five fractions of organic carbon with different molecular weight ranges and chemical polarity. Two major fractions observed are: the hydrophilic chromatographable organic carbon (COC) that elutes from the column, and non-chromatographable organic carbon, which is the hydrophobic organic carbon (HOC) fraction

that binds irreversibly to the hydrophobic solid phase of the column. COC is further fractionated into four major fractions: biopolymers ( $> 20,000$  g/mol), humic substances (1200–500 g/mol), building blocks (weathering product of humic substances) (500–350 g/mol), and low molecular weight (LMW) organics ( $< 350$  g/mol) (Amy et al., 2011; Huber et al., 2011; Shanmuganathan et al., 2015; Velten et al., 2011). The difference between DOC and COC is assumed to be the HOC fraction (Huber et al., 2011).

The LC-OCD uses a Toyopearl TSK HW50S column with a phosphate buffer mobile phase of pH 6.8 at a flow rate of 1.1 mL/min and the injection volumes were 1 mL. The chromatographic column is a weak cation exchange column containing a polymethacrylate solid phase. Calibration of retention times of the DOC fractions was performed using two standards (Suwannee river Standard II humic acid and fulvic acid from the International Humic Substances Society). The ChromCALC software package (DOC-LABOR, Karlsruhe, Germany) specifically designed for the LC-OCD measurement, was used for data acquisition and data processing, and the concentration of each fraction of organic carbon was determined from the chromatogram using a constrained peak-fitting process based on known retention times.

Concentrations of MOPs were determined using solid phase extraction (SPE) followed by high performance liquid chromatograph with tandem mass spectroscopy (HPLC-MSMS) and quantified by isotope dilution. Samples (0.5 L) were collected in glass bottles, stored in the dark ( $< 4$  °C) and extracted within 48 h. Prior to SPE, samples were spiked with 50 ng (50  $\mu$ L of a 1 mg/L solution) of isotope labelled analogues of all target MOPs. Samples were loaded onto pre-conditioned OASIS 500 mg hydrophilic/lipophilic balance cartridges (Waters, Millford, USA) at a rate  $< 10$  mL/min. After completion, cartridges were rinsed with 5 mL of water, dried with a stream of nitrogen and stored at 4 °C if not immediately eluted. Target MOPs were eluted from the cartridges with methanol (3 x 2.5 mL) and 1/9 (v/v)

methanol/methyl-*tert*-butylether (2.5 mL), evaporated under a stream of nitrogen to approximately 100  $\mu$ L. The extract was made up to approximately 1 mL with 60% methanol/water (v/v), transferred to a 2 mL amber auto-sampler vial for instrumental analysis. Target MOPs were chromatographically separated and quantified using an Agilent (Palo Alto, USA) 1200 series high performance liquid chromatograph equipped with a 150 x 4.6 mm, 5  $\mu$ m particle size, Luna C18 column (Phenomenex, Torrence, USA).

Identification and quantification of MOPs was carried out using an API 4000 triple quadrupole mass spectrometer (Sciex/Applied Biosystems, Forster City, USA) equipped with a turbo-V ion source employed in both positive and negative electro-spray modes. A binary gradient consisting of 5 mM ammonium acetate in water (A) and 100% methanol (B) at a flow rate of 800  $\mu$ L/min was used. For ESI positive analyses, the gradient was as follows: 10% B held for 0.50 min, stepped to 50% B at 0.51 min and increased linearly to 100% B by 8 min, then held at 100% B for 2 min. For ESI negative analyses, the gradient was as follows: 10% B held for 0.50 min, stepped to 60% B at 0.51 min and increased linearly to 100% B by 8 min, then held at 100% B for 3 min. A 5 min equilibration step at 10% B was used at the beginning of each run. An injection volume of 10  $\mu$ L was used for all methods. Using scheduled multiple reaction monitoring (sMRM) two precursor – product ion transitions were monitored for all analytes, the most abundant used for quantitation. Calibration was achieved by construction of a minimum 5-point analyte/ISTD relative response ratio over a concentration range 0.5–500 ng/mL. Linearity coefficients for all analytes were  $\geq 0.99$ . Limits of quantification were determined as the concentration which gave a peak of an extracted target analyte with a signal to noise ratio (s/n) of  $> 10$ . For quality assurance and control, laboratory grade water blanks and fortified blanks at 10 and 100 ng/L were extracted with every batch of samples. No analytes were detected in blank samples above the quantitation limit. Recoveries of all target analytes were within 20% of expected concentrations.

Solvents, buffer reagents and analytical standards were purchased from Sigma Aldrich (North Ryde, Australia). Isotope labelled internal standards were purchased from CDN Isotopes (Pointe-Claire, Canada). Water used in analysis was obtained from a Milli-Q purification system (Merck, Darmstadt, Germany).

#### *2.4. Column experiment*

Column adsorption experiments were conducted by passing ROC first through a GAC column and then the effluent from the GAC column through a Purolite column. The columns consisted of 2-cm diameter glass tubes and these were packed to a bed height of 50 cm with 80 g GAC and 122 g Purolite. Crittenden et al. (1986) reported that channelling and wall effects during filtration in columns is minimised if the ratio of column diameter to adsorbent particle size is  $> 50$ . However, McCabe et al. (2004) stated that the column diameter of at least 8 times the packing diameter is required to minimise channelling. In the current study assuming 85% of the particles are between 0.42 and 0.6 mm, the mean size of GAC was around 0.51mm. Thus, the ratio based on the mean particle diameter of GAC is approximately 39, which is much higher than the threshold value of McCabe et al. (2004) but smaller than that of Crittenden et al. (1986). Considering these two studies it is unlikely that significant channelling would have occurred in the current study. Also, in the upward flow of solutions used in the columns in this study, where all particles were in contact with the liquid phase, and trapped air removed, less channelling would have occurred, unlike during down flow experiments.

A stainless-steel sieve was fixed at the bottom of the columns to keep the adsorbents in place. After filling the column with the adsorbents another stainless-steel sieve was placed on top of the bed followed by glass beads to: firstly, avoid expansion of the bed; and secondly, maintain a uniform flow of ROC solution through the columns. ROC solution was

passed upward from the bottom of the GAC column at a flow rate of 40 mL/min (6.31 m/h). Upward flow was used to help in the removal of any trapped air and to cause all particles to interact with the liquid phase with minimal channelling. The effluent from the GAC column was passed through the Purolite column again in an upward flow mode. The flow velocity was maintained using a peristaltic pump. Samples of effluents from the GAC and Purolite columns were collected at 2, 3, 4, 6.5, and 9.5 days, and analysed for DOC and its fractions. The concentrations of MOPs were analysed only in the effluents from the GAC column at 9.5 days. Almost all MOPs were completely removed by the GAC column, and consequently, it was not necessary to analyse the effluents of the Purolite column (only trace amounts entered the Purolite column). Effluents of GAC column at 2, 3, 4, and 6.5 days were also not analysed for MOPs because almost 100% of the MOPs were removed even after 9.5 days of filtration and at shorter time the same amount or even more would have been removed. At shorter times the number of adsorption sites in GAC available for MOPs is higher and therefore, higher percentage of MOPs would have got removed.

### *2.5. Percentage removal and partition coefficient*

Percentage removal and amounts adsorbed of DOC and its fractions, and MOPs were calculated using the following equations (Jamil et al., 2019a; Velten et al., 2011):

$$\% \text{ removal} = 100 [(1 - 1/2 (C_{\text{out},t} + C_{\text{out},t-1}) / C_o]$$

$$q = Q \times \Delta t / m [(C_o - 1/2 (C_{\text{out},t} + C_{\text{out},t-1})]$$

where  $C_o$  is concentration of influent in the columns (DOC, mg/L; MOP, ng/L),  $C_{\text{out},t}$  is effluent concentration at time  $t$  (current sampling time), and  $C_{\text{out},t-1}$  is effluent concentration at time  $t-1$  (previous sampling time) (DOC, mg/L; MOP, ng/L).  $q$  is amounts adsorbed between two consequent times (mg/g GAC or Purolite),  $Q$  is flow rate (L/min),  $\Delta t$  is time interval between the two sampling times (min), and  $m$  is mass of GAC or Purolite in the column (g).

The partition coefficient ( $k_p$ ), which is the ratio of the amount adsorbed to the concentration in solution, was calculated by dividing  $q$  by  $C_{out,t}$ .  $k_p$  is an indicator of the adsorbability of the DOC components on GAC and Purolite (Velten et al., 2011).

### 3. Results and discussion

#### 3.1. DOC and the fractions removed by GAC and Purolite columns

The chromatograms obtained from the LC-OCD analysis described in Section 2.3 for the influent and effluents of the columns at the first three bed volumes are presented in Fig. S1 (Supplementary Data). First three bed volumes are considered here because they represent the initial part of the breakthrough period in the columns where the highest percentages of DOC fractions in ROC are removed. The shapes of the chromatograms are identical to those of untreated and anion exchange resin treated groundwaters reported by Hu et al. (2014). In the untreated ROC sample, all peaks had large height/area (LC-OCD signals), and overlapped each other as observed by Hu et al. (2014). The peaks decreased in height after GAC and Purolite treatments, indicating that significant amounts of the DOC fractions were removed by these treatments. The Purolite effluent samples had lower peak signals than the GAC effluent samples, because GAC + Purolite treatment removed more DOC fractions than the initial GAC alone treatment. A notable feature observed in the chromatograms is that the GAC effluents had the largest peaks for the dominant DOC humics fraction ((Table 1) at 43 min retention time, whereas when the effluent was subsequently passed through Purolite, these peaks disappeared for all bed volumes. This indicates that GAC was able to remove only limited amounts of humics in ROC, but Purolite removed all the residual humics. Biopolymers, which had the lowest concentration in DOC, exhibits the smallest peak (at 32 min retention time). The peak for Purolite is smaller than GAC demonstrating the contributions of both the adsorbents in removing this fraction.

From the concentrations of total DOC and its fractions determined using the LC-OCD



analysis, the removals of DOC and its fractions by the adsorbents in the columns as a percentage of their concentrations in ROC were calculated and presented in Fig. 1. The bottom part of each bar denotes the percentage removed by the GAC column while the top part denotes the percentage contribution to the overall removal of DOC and its fractions by the subsequent Purolite column. The total height of the bars represents the total percentage removals. The results show that the removal percentage of all fractions, decreased when the bed volume (increased time) in the GAC column increased as would be expected in a typical breakthrough curve in column experiments (Patel, 2019). This is due to increased saturation of the available adsorption sites as time progressed, meaning there were fewer sites for subsequent adsorption. In the case of the Purolite column, however, two opposing factors were occurring. The first factor is, as in the case of GAC column, the increased saturation of adsorption sites leaving fewer sites for subsequent adsorption as time progressed which reduces the removal percentage. The second is that the influent concentrations of DOC and DOC fractions into the Purolite column (which are the effluent concentrations from GAC column) increased over time. In the case of the negatively charged humics which had high affinity to the positively charged Purolite, the percentages generally increased, and therefore, the second factor seemed to have dominated. This is also reflected in the hydrophilic fraction and total DOC percentage increases, because both are made up of a higher percentage of humics.

A notable feature of these results is that, despite GAC being the first adsorbent, the percentage of humics fraction removed by GAC was lower than that of Purolite, except for the first bed volume. This is probably because the positively charged hydrophilic Purolite anion exchange resin had strong electrostatic attraction to the negatively charged humics as revealed by the partition coefficient data where humics had a much higher partition coefficient than GAC (Fig. 2). The main mechanism of adsorption here is exchange of negatively charged humics with the chloride ions in the resins (Cornelissen et al., 2008). On

the other hand, GAC has mostly hydrophobic characteristics (Jeirani et al., 2017; Kaur et al. 2018; Valderrama et al. 2009). Furthermore, it possesses negative charges resulting from the ionisation of surface carboxylic and phenolic groups. The zero point of charge (pH at which the net surface charge is zero) of GAC is 3.2, indicating that above this pH the surface charge on GAC is negative (Kalaruban et al., 2019). Both the hydrophobic character and negative charges on GAC are not favourable for the adsorption of humics materials which are mostly negatively charged (Yang et al., 2014). However, these surface groups can form H-bonding with the humics (Ahnert et al., 2003, Moreno-Castilla, 2004) which can help in some adsorption of this fraction. Also, van der Waals force interaction between the humics molecules and GAC surface atoms can promote adsorption (Valderrama et al., 2009).

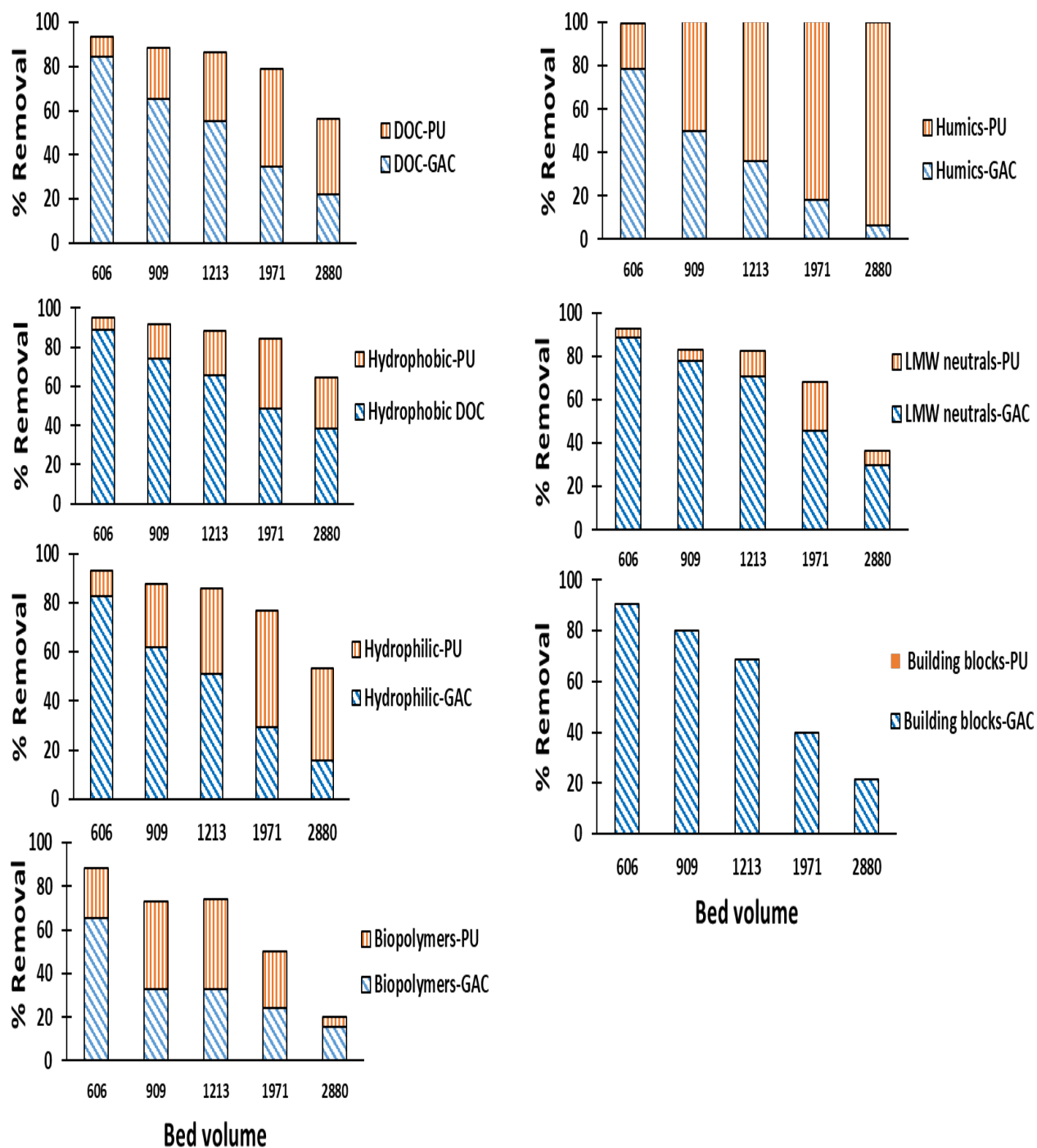
In contrast to Purolite, GAC had a higher preference for the smaller-sized LMW neutrals and building blocks, due to penetration of these fractions into the GAC pores and being adsorbed. This is consistent with the partition coefficient results for these fractions (Fig. 2). Additionally, GAC having predominantly hydrophobic characteristics, adsorbed a greater percentage of the hydrophobic fraction than the hydrophilic Purolite. The hydrophobic interaction is explained as being due to  $\pi$ - $\pi$  bonding between aromatic rings in the hydrophobic molecules in the hydrophobic fraction and GAC surface (Moreno-Castilla 2004; Valderrama et al. 2009). In this type of bonding, oxygen groups on the GAC surface act as electron donors, while the aromatic rings of the hydrophobic molecules act as electron acceptors (Dąbrowski et al., 2005; Tran et al., 2017).

For all the fractions, except the building blocks whose concentration was very small compared to others, a combination of the adsorbents produced better removal (90-100% at 606 bed volumes and 35-100% at 2880 bed volumes ) than when only GAC was used (78-90% at 606 bed volumes and 8-40% at 2880 bed volumes) (Fig. 1). Such a comparison cannot be made for Purolite alone because this adsorbent was sequenced after GAC, and there was no data for Purolite adsorbent alone to compare with the combined adsorbents data. However,

our data from another short-term column study (5-50 bed volumes) where the same Purolite resin was used alone at the same flow velocity to remove DOC fractions of ROC from the same treatment plant, can be applied here to provide this information (Jamil et al., 2019b). In that study, it was found that at the highest bed volume of 50, 10-70% of all the different DOC fractions and total DOC, except humics were removed by Purolite alone. Humics were completely removed (100%). At higher bed volumes the removal percentages are expected to be even lower because less adsorption sites were available. These removal percentages are lower than the removal percentages obtained in the current study at 606 bed volumes for combined adsorbents. Therefore, based on the results presented in Fig. 1 and from the earlier study, it can be concluded that a combination of GAC and Purolite, the former followed by the latter, will remove more DOC and its fractions (except humics which were completely removed by both Purolite alone and combined adsorbents) than when the respective adsorbents are used alone. Another exception is building blocks (concentrations only 10% of total DOC) which was not removed to any significant degree by Purolite after GAC adsorption. A possible reason for this is that building blocks which are breakdown products (hydrolysates) of humics (Cornelissen et al., 2008; Huber et al. 2011; Velten et al., 2011) have low molecular weights and not able to compete with the high molecular weight humic fraction for adsorption on to Purolite. Another reason is that humics concentration was 5-10 times higher than that of building blocks in the GAC effluent which causes ineffective competition with humics for adsorption. A long-term column study is recommended with Purolite column as the first step followed by a GAC column to investigate its relative merits.

In the current study, Purolite was used after GAC, because the latter was found to be a better adsorbent for DOC than the former in our earlier batch adsorption study using the same adsorbents as in this study. GAC had a much higher Freundlich  $k_F$  value ( $\text{mg/g (L/mg)}^{1/n}$ ), that is related to the adsorption capacity, of 2.80 compared to 0.01 for Purolite (Jamil et al., 2019b). Furthermore, in this batch study, when GAC was used prior to Purolite, it removed a

majority of DOC leaving only a small amount to be removed by Purolite. On the other hand, when Purolite was used prior to GAC, the removal by each adsorbent were similar and shared almost equally by each. Additionally, when GAC is used first, due to its hydrophobic properties and porous structure, it can remove the hydrophobic DOC fraction and the low molecular weight fractions in the pores, which might help Purolite, the subsequent column, to remove the other DOC fractions to its full potential with minimum competition from those fractions removed by GAC.



**Fig. 1.** DOC and its fractions removal, firstly by the GAC column and then by the Purolite (PU) column.

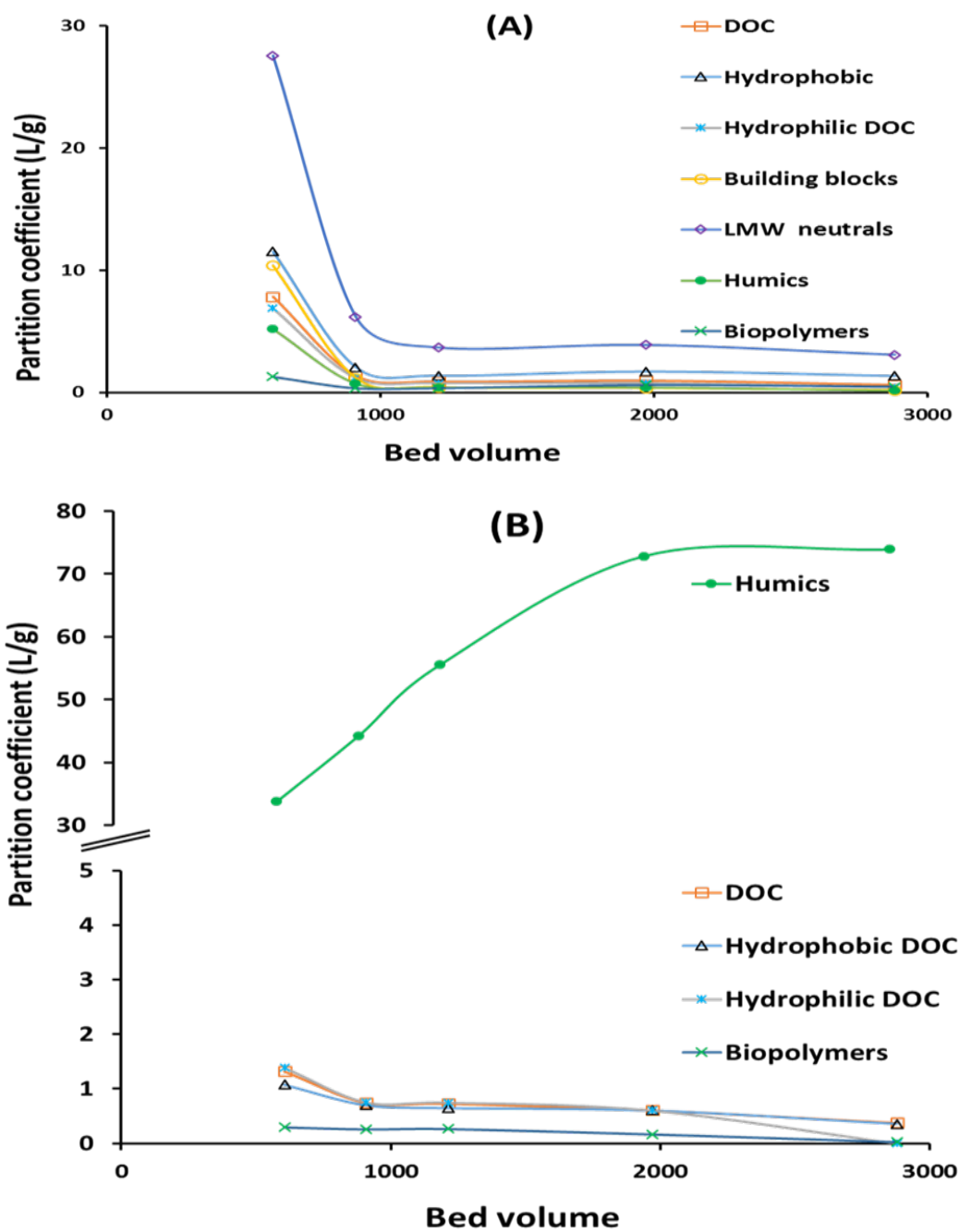


Fig. 2. Partition coefficients of DOC fractions in (A) GAC column and (B) Purolite column.

### **3.2.** *MOPs removal*

Almost all MOPs (95-100%) were removed by GAC at 9.5 days of operation (Table 2). Out of the 17 MOPs tested, 14 MOPs were completely (100%) removed. The high percentage of MOPs removed is due to the high affinity of GAC for MOPs and greater height of the column used in the experiment. Our earlier results demonstrated that MOPs have much higher affinity for GAC than DOC fractions (Jamil et al. 2019a). The present study confirmed this. DOC removal percentages ranged from 5 to 40% at 9.5 days (Fig. 1), which are much lower than the removal percentages (95-100%) of MOPs.

In our earlier study, the percentage of MOPs removed by GAC column ranged from 55-100%, and these removal percentages were found to depend on electrical charge and hydrophobicity of the MOPs (Jamil et al., 2019a). The positive or neutral MOPs with high hydrophobicity ( $\text{Log Kow} > 3.5$ ) had the highest percentage removal and those which are negatively charged, regardless of their degree of hydrophobicity, had the lowest percentage removal. The much higher removal percentages of MOPs observed in the present study, regardless of charge and hydrophobicity of MOPs, is due to the greater height of the GAC column in this study (50 cm) compared to the previous study (8 cm). This is despite the flow velocity being the same in both studies (40 mL/min) and influent MOPs concentrations were approximately the same. The study confirmed that GAC is a useful adsorbent that can be used to continuously remove all MOPs for a lengthy period. The removal efficiency of DOC, on the other hand, declined as time passed and another adsorbent such as Purolite is needed to subsequently remove the DOC that was not removed by GAC.

## **4. Conclusions**

GAC is largely hydrophobic and porous in character and was found to be very effective in removing the hydrophobic and the smaller-sized low molecular weight neutrals and the

building blocks of the hydrophilic fractions of DOC, but it was not effective in removing the hydrophilic humics fraction. However, by passing the effluents of the GAC column through another column containing the anion exchange resin, Purolite, all DOC fractions were effectively removed. With increased bed volumes, the percentage of all DOC fractions removed decreased, but when the GAC effluents were treated with the Purolite column, the removal of these fractions increased with bed volume. In the case of the humics fraction, 100% of it was removed by the combined action of the two adsorbents. The study concluded that combining adsorbents having different affinities towards the DOC fractions will effectively achieve larger amounts of DOC and its components being removed.

All 17 MOPs were almost completely removed by the GAC column even after 9.5 days (2880 bed volumes) of continuous use of this column compared to much less of the DOC fractions being removed. This confirmed that MOPs had much higher adsorption affinity than DOC fractions towards GAC.

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### **References**

- Ahnert, F., Arafat, H.A., Pinto, N.G. 2003. A study of the influence of hydrophobicity of activated carbon on the adsorption equilibrium of aromatics in non-aqueous media. *Adsorption*, 9, 311-319.
- Amy, G.L., Rodriguez, S.G.S., Kennedy, M.D., Schippers, J.C., Remize, P.J., Barbe, C., Manes, C.L.de O., West, N.J., Lebaron, P., van der Kooij, D., Veenendaal, H., Schaule, G., Petrowski, K., Huber, S., Sim, L.N., Ye, Y., Chen, V., Fane, A.G., 2011.



Chapter 1. Water Quality Assessment Tools, Membrane Based Desalination, An Integrated Approach (MEDINA), IWA Publishing Alliance House, London.

- Arola, K., Van der Bruggen, B., Mänttari, M., Kallioinen, M., 2019. Treatment options for nanofiltration and reverse osmosis concentrate from municipal wastewater treatment – A review. *Crit. Rev. Environ. Sci. Tech.*, 49, 2049-2116.
- Bolto, B., Dixon, D., Eldridge, R., 2004. Ion exchange for the removal of natural organic matter. *React. Funct. Poly.*, 60, 171-182.
- Bolto, B., Gregory, J., 2007. Organic polyelectrolytes in water treatment. *Water Res.*, 41, 2301-2324.
- Chingombe, P., Saha, B., Wakeman, R.J., 2005. Surface modification and characterisation of a coal-based activated carbon. *Carbon*, 43, 3132-3143.
- Cooney, D.O., 1999. Adsorption design for wastewater treatment. Lewis Publishers, Boca Raton, Florida.
- Cornelissen, E.R., Moreau, N., Siegers, W.G., Abrahamse, A.J., Rietveld, L.C., Grefte, A., Dignum, M., Amy, G., Wessel, L., 2008. Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions. *Water Res.*, 42, 413-423.
- Crittenden, T.C., Berrigan, J.K., Hand, D.W., 1986. Design of rapid small-scale adsorption tests for a constant diffusivity. *J. Water Pollut. Cont. Fed.*, 58, 312-319.
- Dąbrowski, A., Podkościelny, P., Hubicki, Z., Barczak, M., 2005. Adsorption of phenolic compounds by activated carbon—a critical review. *Chemosphere*, 58, 1049-1070.
- Delgado, L.F., Charles, P., Glucina, K., Morlay, C., 2012. The removal of endocrine disrupting compounds, pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated carbon—A review. *Sci. Total Environ.*, 435-436, 509-525.

- Eeshwarasinghe, D., Loganathan, P., Kalaruban, M., Sounthararajah, D.P., Kandasamy, J., Vigneswaran, S., 2018. Removing polycyclic aromatic hydrocarbons from water using granular activated carbon: kinetic and equilibrium adsorption studies. *Environ. Sci. Pollut. Res.*, 25, 13511-13524.
- Hajibabania, S., Verliefde, A., McDonald, J.A., Khan, S.J., Le-Clech, P., 2011. Fate of trace organic compounds during treatment by nanofiltration. *J. Membr. Sci.*, 373, 130-139.
- Hatt, J.W., Germain, E., Judd, S.J., 2013. Granular activated carbon for removal of organic matter and turbidity from secondary wastewater. *Water Sci. Technol.* 67, 846-853.
- Hu, J., Martin, A., Shang, R., Siegers, W., Cornelissen, E., Heijman, B., Rietveld, L., 2014. Anionic exchange for NOM removal and the effects on micropollutant adsorption competition on activated carbon. *Sep. Purif. Tech.*, 129, 25-31.
- Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size exclusion chromatography-organic carbon detection organic nitrogen detection (LC-OCD-OND). *Water Res.*, 45, 879–885.
- Humbert, H., Gallard, H., Suty, H., Croué, J., 2008. Natural organic matter (NOM) and pesticides removal using a combination of ion exchange resin and powdered activated carbon (PAC). *Water Res.* 42, 1635-1643.
- Ikehata, K., El-Din, M.G., Snyder, S.A., 2008. Ozonation and Advanced Oxidation Treatment of Emerging Organic Pollutants in Water and Wastewater. *Ozone: Sci. Eng.* 30, 21-26.
- Jamil, S., Jeong, S., Vigneswaran, S., 2018. Application of forward osmosis membrane in nanofiltration mode to treat reverse osmosis concentrate from wastewater reclamation plants. *Water Sci. Technol.*, 77, 1990-1997.
- Jamil, S., Loganathan, P., Listowski A., Kandasamy J., Khourshed C., Vigneswaran S. (2019a). Simultaneous removal of natural organic matter and micro-organic pollutants

- from reverse osmosis concentrate using granular activated carbon. *Water Res.*, 155, 106-114.
- Jamil, S., Loganathan, P., Kandasamy, J., Listowski, A., Khoureshed, C., Naidu, R., Vigneswaran, S., 2019b. Removal of dissolved organic matter fractions from reverse osmosis concentrate: Comparing granular activated carbon and ion exchange resin adsorbents. *J. Environ. Chem. Engineer.*, 7, 103126, 8 pages.
- Jeirani, Z., Niu, C.H., Soltan, J., 2017. Adsorption of emerging pollutants on activated carbon. *Rev. Chem. Engineer.*, 33, 491-522.
- Kalaruban, M., Loganathan, P., Nguyen, T.V., Nur, T., Hasan Jahir, M.A., Nguyen, T.H., Trinh, M.V., Vigneswaran, S., 2019. Iron-impregnated granular activated carbon for arsenic removal: Application to practical column filters. *J. Environ. Manage.*, 239, 235-243.
- Kaur, H., Bansiwala, A., Hippargi, G., Pophali, G.R., 2018. Effect of hydrophobicity of pharmaceuticals and personal care products for adsorption on activated carbon: Adsorption isotherms, kinetics and mechanism. *Environ. Sci. Pollut. Res.*, 25, 20473-20485.
- Kazner, C., Lehnberg, K., Kovalova, L., Wintgens, T., Melin, T., Hollender, J., Dott, W., 2008. Removal of endocrine disruptors and cytostatics from effluent by nanofiltration in combination with adsorption on powdered activated carbon. *Water Sci. Technol.*, 58, 1699-1706.
- Kennedy, A.M., Reinert, A.M., Knappe, D.R.U., Ferrer, I., Summers, R.S., 2015. Full- and pilot-scale GAC adsorption of organic micropollutants. *Water Res.*, 68, 238-248.
- Korotta-Gamage, S.M., Sathasivan, A., 2017. A review: potential and challenges of biologically activated carbon to remove natural organic matter in drinking water purification process. *Chemosphere*, 167, 120-138.

- Li, X., Hai, F.I., Nghiem, L.D., 2011. Simultaneous activated carbon adsorption within a membrane bioreactor for an enhanced micropollutant removal. *Bioresource Tech.*, 102, 5319-5324.
- Loftsson, T., Hreinsdóttir, D., Másson, M., 2005. Evaluation of cyclodextrin solubilization of drugs. *Int. J. Pharm.*, 302, 18-28.
- Matilainen, A., Vepsäläinen, M., Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment: A review. *Adv. Colloid Interface Sci.*, 159, 189-197.
- McCabe, W.L., Smith, J.C., Harriott, P., 2004. *Unit Operations of Chemical Engineering*. McGraw-Hill Inc., New York.
- Mohiuddin, A., Rajanayagam, C., Kearney, C., 2014. Optimisation of non-ionic polymer to address production issues with high-colour low-turbidity raw water. A report of five events at Sydney Water's Nepean Water Filtration Plant to compare plant performance before and after optimisation. *Water*, 41, 58-63.
- Moreno-Castilla, C., 2004. Adsorption of organic molecules from aqueous solutions on carbon materials. *Carbon*, 42, 83-94.
- Pal, A., Gin, K.Y.H., Lin, A.Y.C., Reinhard, M., 2010. Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. *Sci. Total Environ.*, 408, 6062-6069.
- Patel, H., 2019. Fixed-bed column adsorption study: a comprehensive review. *Appl. Water Sci.*, 9, 45 (17 pages).
- Roberts, D.A., Johnston, E.L., Knott, N.A., 2010. Impacts of desalination plant discharges on the marine environment: A critical review of published studies. *Water Res.*, 44, 5117-5128.

- Serrano, D., Suárez, S., Lema, J.M., Omil, F., 2011. Removal of persistent pharmaceutical micropollutants from sewage by addition of PAC in a sequential membrane bioreactor, *Water Res.*, 45, 5323-5333.
- Shanmuganathan, S., Loganathan, P., Kazner, C., Johir, M.A.H., Vigneswaran, S., 2017. Submerged membrane filtration adsorption hybrid system for the removal of organic micropollutants from a water reclamation plant reverse osmosis concentrate. *Desalination*, 401, 134-141.
- Shanmuganathan, S., Nguyen, T.V., Jeong, S., Kandasamy, J., Vigneswaran, S., 2015. Submerged membrane – (GAC) adsorption hybrid system in reverse osmosis concentrate treatment. *Sep. Purif. Technol.*, 146, 8-14.
- Shanmuganathan, S., Nguyen, T.V., Shim, W.G., Kandasamy, J., Listowski, A., Vigneswaran, S., 2014. Effluent organic matter removal from reverse osmosis feed by granular activated carbon and purolite A502PS fluidized beds. *J. Indust. Engineer. Chem.*, 20, 4499-4508.
- Snyder, S.A., Adham, S., A., Redding, A.M., Cannon, F.S., De Carolis, J., Oppenheimer, J., Wert, E.C., Yoon, Y., 2007. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. *Desalination*, 202, 156–181.
- Snyder, S.A., Wert, E.C., Rexing, D.J., Zegers, R.E., Drury, D.D., 2006. Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone: Sci. Eng.* 28, 445-460.
- Summers, R.S., Roberts, P.V., 1988. Activated carbon adsorption of humic substances. II. Size exclusion and electrostatic interactions. *J. Colloid Interface Sci.* 122, 382-397.
- Ternes, T.A., Joss, A. (Eds.), 2006. *Human Pharmaceuticals, Hormones and Fragrances - The Challenge of Micropollutants in Urban Water Management*. IWA Publishing, London.

- Tran, H.N., Wang, Y.F., You, S.J., Chao, H.P., 2017. Insights into the mechanism of cationic dye adsorption on activated charcoal: The importance of  $\pi$ - $\pi$  interactions. *Process Saf. Environ. Prot.*, 107, 168-180.
- Valderrama, C., Gamisans, X., Cortina, J.L., Farrán, A., De las Heras, F.X., 2009. Evaluation of polyaromatic hydrocarbon removal from aqueous solutions using activated carbon and hyper-crosslinked polymer (Macronet MN200). *J. Chem. Technol. Biotechnol.*, 84, 236- 245.
- Velten, S., Knappe, D.R.U., Traber, J., Kaiser, H., von Gunten, U., Boller, M., Meylan, S., 2011. Characterisation of natural organic matter adsorption in granular activated carbon adsorbers. *Water Res.*, 45, 3951-3959.
- Wang, W., Gu, P., Zhang, G., Wang, L., 2013. Organics removal from ROC by PAC accumulative counter current two-stage adsorption-MF hybrid process – A laboratory-scale study. *Sep. Purif. Tech.*, 118, 342-349.
- Wang, J., Wang, S., 2016. Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: A review. *J. Environ. Manage.*, 182, 620-640.
- Westerhoff, P., Yoon, Y., Snyder, S., Wert, E., 2005. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ. Sci. Technol.*, 39, 6649-6663.
- Yang, X., Flowers, R.C., Weinberg, H.S., Singer, P.C., 2011. Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. *Water Res.*, 45, 5218-5228.
- Yang, Z., Li, H., Yan, H., Wu, H., Yang, H., Wu, Q., Li, H., Li, A., Cheng, R., 2014. Evaluation of a novel chitosan-based flocculant with high flocculation performance, low toxicity and good floc properties. *J. Hazard. Mater.*, 276, 480-488.

Yangali-Quintanilla, V., Sadmania, A., McConville, M., Kennedy, M., Amy, G., 2009.

Rejection of pharmaceutically active compounds and endocrine disrupting compounds by clean and fouled nanofiltration membranes. *Water Res.* 43, 2349-2362.

Ye, N., Cimetiere, N., Heim, V., Fauchon, N., Feliers, C., Wolbert, D., 2019. Upscaling fixed bed adsorption behaviors towards emerging micropollutants in treated natural waters with aging activated carbon: Model development and validation. *Water Res.*, 148, 30-40.

Zhou, T., Lim, T., Chin, S., Fane, A.G., 2011. Treatment of organics in reverse osmosis concentrate from a municipal wastewater reclamation plant: Feasibility test of advanced oxidation processes with/without pretreatment. *Chem. Eng. J.*, 166, 932-939.

## Supplementary Data

### Removal of organic matter from wastewater reverse osmosis concentrate using granular activated carbon and anion exchange resin adsorbent columns in sequence

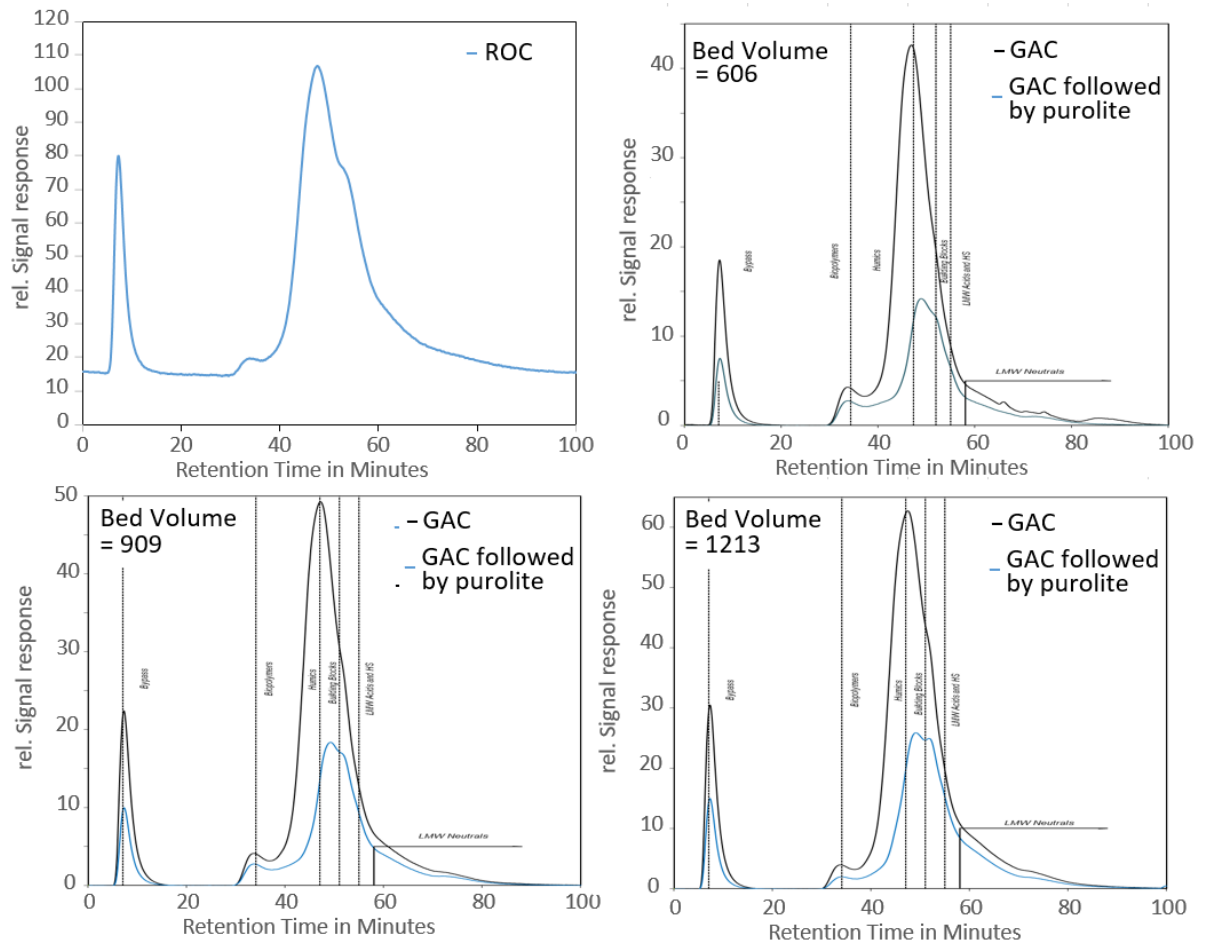
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**Fig. S1.** LC\_OCD chromatograms for initial ROC and various DOC fractions after GAC column and Purolite column treatments at different bed volumes (GAC f.by PU refers to GAC followed by Purolite)