

Performance evaluation of organic matter adsorption from actual graywater using GAC: Orbitrap™ MS and optimization

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Abstract. The complex combination of organic contaminants in the wastewater made water treatment challenging; hence, organic matter in water bodies is usually measured in terms of organic carbon. Since it is important to identify the types of compounds when deciding suitable treatment methods, this study implemented a quantitative and qualitative analysis of the organic matter content in an actual graywater sample from Ulsan, Republic of Korea using mass spectroscopy (MS). The graywater was treated using adsorption to remove the organic contaminants. Using orbitrap MS, the organic matter content between an untreated graywater and the treated effluent were compared which yielded a significant formula count difference for the samples. It was revealed that CHON formula has the highest removal count. Isotherm studies found that the Freundlich equation was the best fit with a coefficient of determination (R^2) of 0.9705 indicating a heterogeneous GAC surface with a multilayer characteristic. Kinetics experiments fit the pseudo-second order equation with an R^2 of 0.9998 implying that chemisorption is the rate-determining step between the organic compounds and GAC at rate constant of 52.53 g/mg·h. At low temperatures, the reaction between GAC and organic compounds were found to be spontaneous and exothermic. The conditions for optimization were set to achieve a maximum DOC and TN removal which yielded removal percentages of 94.59% and 80.75% for the DOC and TN, respectively. The optimum parameter values are the following: pH 6.3, 2.46 g of GAC for every 30 mL of graywater sample, 23.39 hrs contact time and 38.6°C.

Keywords: GAC adsorption; organic matter contaminant; Orbitrap MS analysis

1. Introduction

The complex mixture of organic compounds in domestic wastewater made it difficult to identify which types of compounds were removed using various wastewater treatment methods (Barber *et al.* 2013, Talarposhti, Donnelly and Anderson 2001). Aside from the organic components, the presence of inorganic chemicals and heavy metals were also highly possible (Eriksson, Auffarth, Henze and Ledin 2002). Some pollutants are also reactive which made it more challenging when applying various characterization methods. The characterization of the wastewater is integral to the selection of the appropriate treatment method.

Due to its complexity, domestic wastewater is often measured by its organic carbon content such as dissolved organic carbon (DOC) and total organic carbon (TOC) as

well as nutrient concentration, nitrogen (N) and phosphorus (P). DOC and TOC are the most common water quality measures for organic carbon content and indicators for the risk of oxygen depletion (Eriksson *et al.* 2002). These parameters are nonspecific indicators that are often applied for wastewater monitoring standards since these are easy to implement (Cao *et al.* 2012, Majer and Swain 1978). Though these parameters are significant factors for characterizing dissolved organic matter (DOM) in wastewater, it is equally important to understand how certain types of organic compounds respond to wastewater treatment methods. This can be achieved by implementing appropriate techniques for the characterization of the wastewater and treated effluent. The heterogeneous property of DOM in actual wastewaters made the characterization techniques more complicated and challenging. Some of the chemical analyses implemented to characterize DOM are the following: Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), synchronous-scan fluorescence (SF) spectra and mass spectroscopy (MS) (He *et al.* 2014, Lv *et al.* 2016).

Mass spectroscopy (MS) is an effective means for applications that require quantitative and qualitative analysis (El-Aneed, Cohen and Banoub 2009). This method has been widely used for life and health sciences. MS has also been gaining popularity in the environmental sector in

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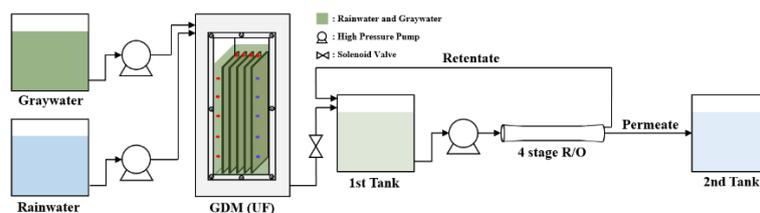


Fig. 1 Science Cabin water treatment facility in Ulsan National Institute of Science and Technology, Republic of Korea

the last two decades (Hernández *et al.* 2012). Most environmental applications focused on quantifying the organic contaminants found in various types of wastewater, with pharmaceutical wastewater as the most common application (Bijlsma, Emke, Hernández and de Voogt, 2012, 2013, Kosjek and Heath 2008, Wang and Gardinali 2014). Some examples of commonly used equipment for MS are the Fourier transform ion cyclotron resonance MS (FT-ICR-MS) and the Orbitrap MS. Between these two apparatus, Orbitrap MS was reported to be less expensive compared to FT-ICR-MS when it comes to wastewater characterization and is more suitable for initial identification of complex organic contaminants (Mangal, Stock and Guéguen 2016). Few works related to domestic wastewater treatment had investigated on specific compounds. Ahmed *et al.* (2014) applied liquid chromatography–electrospray – Orbitrap MS on identifying the transformation products of specific pesticides and pharmaceuticals which were then removed by photo-Fenton process (Ahmed, Brienza, Goetz and Chiron 2014). On the other hand, Schollée *et al.* (2015) used the non-target approach of MS to analyze a biologically-treated wastewater (Schollée, Schymanski, Avak, Loos and Hollender 2015). Another environmental application was to identify emerging contaminants in the wastewater using high-resolution MS which was implemented by Picó and Barceló (2015) (Picó and Barceló 2015). In the same work, they emphasize on the potential of MS equipment for unknown identification in the water environment based on accurate-mass measurements. Previous investigations had established the powerful ability of MS in handling complex wastewater. In this regard, it is important to explore other types of wastewater and treatment methods.

This study conducted a wastewater treatment method to actual graywater samples from domestic and office sources then applied high-resolution MS to compare the untreated and treated samples. Applying high-resolution MS to assess the performance of the wastewater treatment process can be advantageous for highly heterogenous graywater samples. The samples in this study were obtained from a pilot-scale wastewater treatment facility (Fig. 1) which incorporated the gravity-driven membrane (GDM) technology as pretreatment to reverse osmosis. However, the organic removal capacity of GDM is low, bringing more organic contaminants to the 4-stage RO which hastens membrane fouling (Jiang, Zhang, Yan and Wu 2018, Rojas-Serrano *et al.* 2015). To address this issue, adsorption using granular activated carbon (GAC) was explored as an additional graywater treatment process. GAC adsorption has been established as an effective method in removing organic

contaminants from wastewater (Khaleel *et al.* 2015, Xing, Ngo, Kim, Guo and Hagare 2008). Previous studies reported that GAC can reach high removal efficiencies of up to 99% for DOC (adsorption capacity range: 1.0 to 45.8 mg DOC/g GAC) and 30% to 70% for TN (Gur-Reznik, Katz and Dosoretz 2008, Nguyen, Hai, Kang, Price and Nghiem 2012, 2013, Xing *et al.* 2008). In this regard, this study implemented GAC adsorption as a wastewater pretreatment process to reduce the organic contaminants in an actual graywater.

The efficiency of GAC adsorption can be affected by multiple parameters including GAC dosage, contact time and temperature. This study used the self-organizing map (SOM) to explore the effect of the parameters on removing organic contaminants. This technique has been applied in a wastewater treatment for characterizing the composition of dissolved organic matter (Yu *et al.* 2014), predicting TOC removal in a treated water sample (Bieroza, Baker and Bridgeman 2011) and monitoring a wastewater treatment facility (López García and Machón González 2004).

The objectives of this study were to optimize the GAC adsorption process and to assess its performance using a high-resolution MS and SOM. To achieve an optimized removal of organic matter, the specific objectives of this study include the following: a) to determine the effects of varying parameters (GAC dosage, contact time and temperature) on the removal of DOC and TOC, b) to apply adsorption studies (isotherm, kinetics and thermodynamics) between GAC and organic contaminants, c) to optimize and explore the effects of parameters to achieve high DOC and TN removal using a circumscribed central composite (CCC) experimental design and SOM and d) to characterize the organic content of untreated graywater and treated effluent using high-resolution MS. The results of this study can broaden the understanding on which type of organic compounds can be removed at specific parametric conditions.

2. Materials and methods

2.1 Graywater sample

Graywater samples were taken from the Science Cabin of Science Walden (<http://sciencewalden.org/>) at Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea (35° 34' 20.37" N, 129° 11' 12.17" E). The Science Cabin is a research center in UNIST that allows visitors to learn more about scientific technology that highlights the effects of anthropogenic

actions to the environment and society. The cabin includes a water treatment facility that utilizes gravity-driven membrane (GDM) and a four-stage reverse osmosis technology to produce potable water from UNIST graywater. Fig. 1 shows the schematic diagram of the water treatment system from the graywater and rainwater collecting tanks to the reverse osmosis permeate tank.

Here, the cabin collects the wastewater from the residences and offices which are then stored in the graywater tank. The graywater obtained for the GAC adsorption was directly sourced from the graywater tank shown in Fig. 1. To prepare the samples for the adsorption experiments, the graywater was filtered through 1.2 μm pore size of a glass microfiber filter (GF/C, Whatman) and stored in a 4°C refrigerator when not in use. The samples were then characterized to obtain information on pH, DOC, TN and the types of organic contaminants.

2.2 Granular activated carbon

Granular activated carbon (GAC) from Samchully Carbotech, Republic of Korea was used as the adsorbent. The adsorbent was characterized to obtain its physical and elemental properties. Brunauer-Emmett-Teller (BET) surface area analysis was performed using ASAPTM 2420 system (Micrometrics, USA) to evaluate the surface area and surface porosity of GAC. The Barrett-Joyner-Halenda (BJH) method was also applied for the pore size distribution. For the surface morphology of GAC, the scanning electron microscope (SEM) was able to capture the surface images using the Hitachi SU8220 (Japan).

2.3 Organic matter analysis

The organic matters present in the raw and treated graywater were characterized. A total organic carbon analyzer (Shimadzu TOC-VCPH) was used to measure the dissolved organic carbon (DOC) and total nitrogen (TN) before and after adsorption. The water samples were collected into 40-mL sterilized glass vials, which were then placed into the Shimadzu ASI-V autosampler. Each sample was measured thrice to obtain the average TOC and TN values.

To determine the types and quantity of organic compounds present before and after the adsorption, dissolved organic matter (DOM) was extracted from the raw and treated samples using the Oasis Hydrophilic-Lipophilic-Balanced (HLB) solid-phase extraction (SPE) method. The Oasis HLP SPE generic method utilizes the Oasis HLB SPE cartridges (Waters, USA) that contained sorbents for extracting DOM in the water samples during elution.

The SPE method was based on the procedure from Baek *et al.* (Baek, Lee, Park and Cho 2019). Before starting the elution process of DOM, the SPE cartridges were conditioned with 5 mL methanol which was then washed with 10 mL of deionized (DI) water. A 500-mL volume of the actual graywater sample was then pumped into the cartridge using a vacuum pump to a rate of 15 mL/min. This step enables the sorbent in the cartridge adsorbed the DOM.

Table 1 Specifications of the liquid chromatography of the Orbitrap mass spectroscopy (MS)

Ultra-Performance Liquid Chromatography specifications		
Column	Xbrige C18 (2.1 x 50mm, 3.5 μm)	
Flow rate	0.2 mL/min	
Mobile phase	A = water with 0.1% formic acid B = Methanol with 0.1% formic acid	
Gradient program		
Time (min)	Mobile phase A (%)	Mobile phase B (%)
0	90	10
0 – 4	50	50
4 – 17	5	95
17 – 25	5	95
25 – 25.1	90	10
25.1 – 29	90	10

Table 2 Operational parameters of the Orbitrap MS

MS operational parameters	Range or Value	Unit
Spray voltage [+/-]	3800/3000	V
Capillary temperature	320	°C
Sheath gas flow rate	45	-
Aux gas flow rate	10	-
Sweep gas flow rate	2	-
Heat temperature (°C)	300	°C
Full MS		
Mass range	100 – 1,500	m/z
Resolution	140,000	-
AGC target	1,000,000	-
Maximum injection time	100	Ms
Data dependent MSMS (Top 5)		
Resolution	17,500	-
AGC target	500,000	-
Maximum injection time	50	ms

The DOM was then eluted from the sorbent using 6 mL ethyl acetate/methanol (50:50 v/v) with 0.5% ammonia and 3 mL ethyl acetate/methanol (50:50 v/v) with 1.7% formic acid. The eluted sample was collected in a test tube and was then dried by introducing nitrogen gas into the tube to concentrate the sample until the final volume was lowered to 1 mL. To hasten the evaporation of the solvent, the bottom of the test tube was submerged in a water bath at 35°C. This procedure was also conducted for the treated effluent.

The unknown organic contaminants in the concentrated samples were then analyzed using the Ultimate 300 Ultra-Performance Liquid Chromatography (UPLC, Thermo Fisher Scientific, USA) coupled to Q ExactiveTM Plus Hybrid Quadrupole-OrbitrapTM Mass Spectrometer (MS) (Thermo Fisher Scientific, USA). The Orbitrap MS was equipped with a heated electrospray interphase (HESI) for its negative and positive modes. Tables 1 and 2 show the

specifications of the UPLC and the operational parameters of the Orbitrap MS, respectively. The organic compounds were classified and quantified according to their elemental compositions of carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and sulfur (S). The ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) for each molecular formula were plotted in Krevelen diagrams.

2.4 Batch adsorption experiments

Equilibrium, kinetic and thermodynamic studies were conducted for the batch adsorption experiments. 125 mL-Erlenmeyer flasks were used to contain the 30-mL raw graywater and GAC. The flasks were agitated at 50 rpm in a temperature-controlled shaking incubator (WIS-30, Wisecube). Varying dosages of GAC from 0.1 g to 1.0 g at 0.1 g increments were added in the flasks for the equilibrium studies and were shaken for 24 hrs at 25°C. For the kinetic studies, the dosage of GAC remained constant at 1.0 g for each time-step while the temperature was set at 25°C. Each flask was taken after a predetermined time (5 min to 24 hrs). The temperature was also varied to conduct the experiments for thermodynamic studies. The flasks containing the raw graywater and 1.0 g of GAC were subjected to five different temperatures from 25°C to 45°C. After which, the flasks were agitated for 24 hrs. All samples were filtered using a GF/C Whatman filter and were analyzed for DOC and TN concentrations. The pH levels of the samples were also adjusted prior to the adsorption experiments.

The adsorption capacity at equilibrium (q_e , mg DOC/g GAC) was calculated using the following equation

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (1)$$

where, C_0 and C_e are the DOC or TN concentrations at initial and equilibrium (mg/L), respectively; V is the volume of the water sample (L); and, W is the dosage of GAC used for each water sample (g).

For the adsorption capacity at time t (q_t , mg DOC/g GAC), the equation below was used for the kinetic study calculations

$$q_t = \frac{(C_0 - C_t) \times V}{W} \quad (2)$$

where, C_t is the DOC or TN concentration at time t .

2.5 Optimization experiments

Four independent parameters were included for the optimization studies: pH, dosage of adsorbent, contact time and temperature. The MATLAB function for a 5-level circumscribed central composite design (CCD) was applied to generate a total of 36 runs for the optimization experimental design shown in Table A1. CCD was then able to determine the significance and interactions between the parameters corresponding to the DOC and TN removal using a second-order polynomial equation (Ligaray, Futralan, de Luna and Wan 2018, Son, Vavra and Forbes 2015)

$$y = \sum_{j=1}^4 \beta_{ii} x_i^2 + \sum_{i=1}^4 \sum_{j=1}^4 \beta_{ij} x_i x_j + \sum_{j=1}^4 \beta_j x_j + \beta_0 \quad (3)$$

where, y is the response variable (DOC or TN); x_i and x_j are the independent variables (pH, GAC dosage, contact time and temperature); and β_{ii} , β_{ij} , β_j and β_0 are the constant coefficients of the quadratic, interaction, linear and intercept terms, respectively. After obtaining the removal percentages of DOC and TN, Design Expert version 11 (Stat-Ease, Inc., USA) was utilized for the optimization analysis. The analysis of variance (ANOVA) was employed to confirm the significance of the resulting model, wherein p-values of less than 0.0500 for the model terms indicate significance while p-values greater than 0.1000 are insignificant.

2.6 Self-organizing map

The self-organizing map (SOM) was applied for analyzing the effect of parameters on DOC and TN removals, using the MATLAB toolbox (MathWorks, USA). This technique has been used in environmental engineering to characterize the relationship among parameters (García and González 2004, Yu *et al.* 2014). SOM is an unsupervised machine learning technique that clusters similar input samples and presents them on a discrete lattice map (Kim *et al.* 2015). We can assess the associations between variables by comparing their respective SOM maps which have the same topological structures (Kaltch, Hiorth and Bemdtsson 2008, Ye, Cai, Liu and Cao 2009). Each map unit was represented with a weight vector. An input sample was allocated to its best matching unit (BMU) whose weight was the closest to the sample vector. The weight vector of BMU was iteratively updated during the training algorithm. The BMU (c_j) of each sample vector was calculated as

$$c_j = \arg \min_i \{ \|w_i - x_j\| \} \quad (4)$$

where, x_j is the sample vector ($j=1, 2, \dots, n$), n is the number of input samples, w_i is the weight vector ($i=1, 2, \dots, m$), m is the number of map units and $\| \cdot \|$ is the distance measure (i.e., Euclidean distance).

3. Results and discussion

3.1 Characterization

3.1.1 GAC: SEM, BET and BJH

SEM captured the surface morphology of the commercial-grade GAC samples as shown in Fig. 2. The figure shows an enlarged GAC surface at a 3000x magnification, exposing a highly porous surface with various pore sizes from the microporous (> 2.0 nm) and mesoporous (2.0 nm – 50.0 nm) ranges (Sing *et al.* 2008). Table 3 shows the pore size distribution, specific surface area and pore volume of GAC which were determined using the BET and BJH analyses. The BET surface area of GAC was found to be 952.85 m²/g, which is within the

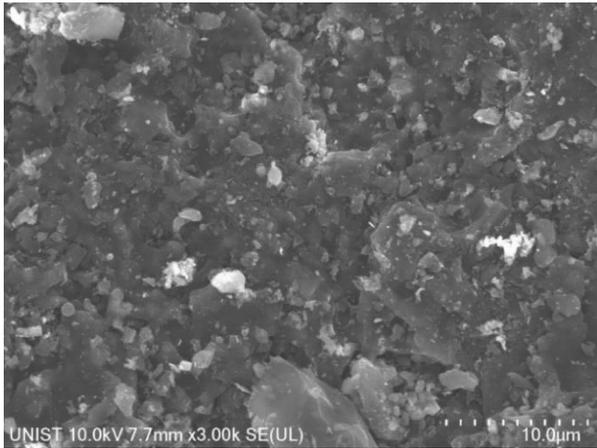


Fig. 2 Granulated activated carbon under the scanning electron microscope (SEM) at 3000x magnification

usual surface area range of activated carbon (900 to 1400 m²/g) (Alighardashi, Pakan, Jamshidi and Shariati 2017, Saka 2012). On the other hand, the BJH test revealed the pore distribution of GAC, yielding a BJH desorption cumulative pore surface area of 292.33 m²/g and a BJH total pore volume of 0.18 cm³/g. Specific pore surface areas and pore volumes for the macropores, mesopores and micropores of the submitted GAC samples are also listed in Table 3. The BJH desorption average pore width was also obtained at 2.59 nm. This result can be classified under the mesoporous group according to the pore size classification of the International Union of Pure and Applied Chemistry (IUPAC) (Sing *et al.* 2008). Previous studies on activated carbon, either commercial or made from various resources, also reported similar values obtained from the BET and BJH analysis. Upadhyayula *et al.* (2009) characterized a commercial-grade activated carbon and reported a BJH pore volume of 0.17 cm³/g and a BJH median pore width of 3.77 nm (mesoporous) (Upadhyayula, Deng, Smith and Mitchell 2009). The results from the commercial-grade activated were synonymous with the values obtained from the BJH tests for activated carbon from indigenous materials such as acorn shells (BJH desorption average pore width: 2.279 nm – 3.033 nm (Saka 2012)) and mulberry tree twigs (BJH desorption average pore width: 2.26 nm – 2.44 nm; volume: 0.24 cm³/g (Tang, Liu and Chen 2012)).

3.1.2 Graywater and effluents: DOC and TN

Wastewater treatment for real graywater in UNIST was investigated in the Science Cabin of UNIST, Republic of Korea; however, removal of organic materials during pretreatment using GDM has been met with challenges, especially regarding maintenance. In the water treatment facility (Fig. 1), raw graywater is collected into the GDM tank, where an ultrafiltration membrane is held. Graywater passes through the membrane; thus, producing the GDM-treated effluent stored in the 1st tank. The effluent in the 1st tank is then pumped towards the 4-stage RO which produces the RO permeate that will be stored in the 2nd tank. For comparison, the DOC and TN concentrations of the raw graywater, GDM-treated effluent and reverse osmosis (RO) permeate from the water treatment facility

Table 3 Surface area and pore analyses of the granulated activated carbon (GAC) using Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods

Measured parameter	Units	Values
BET surface area	m ² /g	952.85
BJH Desorption cumulative pore surface area	m ² /g	292.33
[macropores; mesopores; micropores]		[0.39; 156.42; 110.24]
BJH Desorption average pore width	nm	2.59
BJH total pore volume	cm ³ /g	0.18
[macropores; mesopores; micropores]		[0.0066; 0.12; 0.051]

of the Science Cabin were determined. It was found that the raw graywater had DOC and TN values of 17.06 mg/L and 28.21 mg/L, respectively. The GDM-treated effluent had 15.01 mg/L and 12.13 mg/L while the RO permeate had 1.73 mg/L and 1.78 mg/L for DOC and TN. The measurements obtained show a low removal (12.02%) of DOC from the raw graywater after passing the GDM tank while an expected high removal was observed after the RO process (89.86% from initial). This signifies that the major removal of DOC occurred during the RO process which could be attributed to the molecular size of most DOC substances in the raw graywater that were small enough to pass through the GDM. In this regard, the RO apparatus must have experience considerable stress in removing the bulk of the DOC as compared to GDM. On the other hand, GDM was able to remove an adequate amount of TN substances since less than half of the initial TN concentration remained in the GDM-treated effluent. This was then further reduced by the RO membrane until it reached a total of 93.69% removal of TN from the initial concentration.

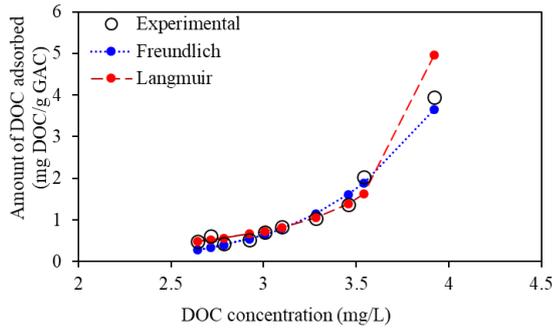
3.2 Adsorption experiments

3.2.1 Isotherm models

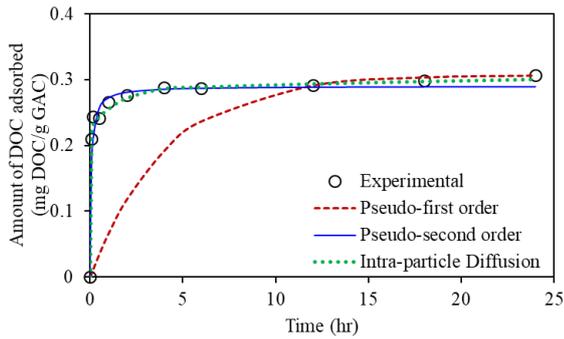
The dosage of GAC was varied from 0.10 g to 1.0 g for each flask at an increment of 0.10 g. All flasks containing the raw graywater samples and GAC were agitated at 50 rpm and subjected to 24 hrs of contact time under 25°C. The resulting DOC concentrations were then fitted into three isotherm models: Langmuir, Freundlich and Dubinin-Radushkevich (D-R). Isotherm models can describe how the target molecules adhere and interact with the adsorbent (Ghaee and Zerafat, 2016, Lee, Jutidamrongphan, Lee and Park, 2017). Langmuir isotherm assumes a homogenous adsorbent surface wherein each active site can only capture one target molecule, hence, creating a saturated monolayer (Ligaray *et al.* 2018, Q.S. Liu, Zheng, Wang, Jiang and Li, 2010). Eq. (5) below shows the Langmuir isotherm (Y. Liu and Shen 2008)

$$q_e = q_{max} \frac{C_e K_L}{C_e K_L + 1} \quad (5)$$

where, C_e is the DOC concentration at equilibrium (mg/L); q_e and q_{max} are the adsorption capacities of GAC at



(a) Freundlich, Langmuir and Dubinin-Radushkevich isotherm models



(b) Pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models

Fig. 3 Isotherm and kinetic studies of the adsorption of dissolved organic carbon (DOC) using granulated activated carbon

equilibrium and maximum (mg GAC/g GAC), respectively and, K_L is the Langmuir constant (-). On the other hand, Freundlich isotherm is an empirical equation that assumes a heterogeneous adsorbent surface (Hameed, Salman and Ahmad 2009, Q.S. Liu *et al.* 2010). This isotherm is expressed by the following equation

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

where, K_F is the Freundlich constant for adsorption capacity (mg DOC/g GAC) and n is the adsorption intensity of the target molecule on the adsorbent (-). The D-R isotherm was the final model applied for the isotherm studies. This model can demonstrate the adsorption mechanism in terms of Gaussian energy distribution, most commonly of organic materials in porous solids (Dada, Olalekan, Olatunya and Dada 2012, Ligaray *et al.* 2018). The equation below describes the D-R isotherm model:

$$\ln q_e = \ln q_{max} - K_{DR} \varepsilon^2 \quad (7)$$

$$\varepsilon = RT \ln \left(1 - \frac{1}{C_e} \right) \quad (8)$$

$$E = - \frac{1}{\sqrt{2K_{DR}}} \quad (9)$$

where, K_{DR} is the D-R constant (kJ^2/mol^2), ε is the Polanyi potential, R is the universal gas constant ($\text{kJ}/\text{mol}\cdot\text{K}$) and E is the mean energy of adsorption (kJ/mol).

Fig. 3a shows the comparison between the predicted DOC values using the Langmuir and Freundlich equations and the experimental values. The results from the equilibrium studies fit the Freundlich isotherm model with a coefficient of determination (R^2) of 0.9705, which is higher than Langmuir's (0.9654) and D-R's (0.9495). This indicates that the surface of GAC has a heterogeneous multilayer characteristic with interactions between its functional groups.

3.2.2 Kinetic models

The kinetics of adsorption was also determined by varying the contact time between the target molecules and GAC while keeping the temperature (25°C), dosage of GAC (1.0 g) and agitation speed (50 rpm) constant. Three commonly applied kinetic equations were compared to identify the rate-determining step of the adsorption process: pseudo-first order (Lagergren), pseudo-second order and intraparticle diffusion. The pseudo-first order equation refers to the physisorption as the rate-determining step (Khan *et al.* 2018, Varma and Misra 2016). This equation is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (10)$$

where, k_1 is the rate constant for the pseudo-first order (1/h) and t is the contact time. The second rate-determining step considered was chemisorption which can be determined by the pseudo-second order equation below (Khan *et al.* 2016)

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (11)$$

where, k_2 is the rate constant for the pseudo-second order ($\text{g}/\text{mg}\cdot\text{h}$). Another rate-determining step is a diffusion-controlled process in which the target molecules diffuse into the interiors of the adsorbent (Doğan and Alkan 2003, Doğan, Alkan, Türkyilmaz and Özdemir 2004). This process can be explained by the intraparticle diffusion mechanism using the following equation

$$q_t = k_i t - c \quad (12)$$

where, k_i is the intraparticle diffusion rate constant and c is the intercept.

The result of kinetics experiment was well fitted to the pseudo-second order reaction model as shown in Fig. 3b, which showed the highest R^2 as 0.9998. This implies that chemisorption is the rate-determining step of the adsorption between the organic compounds in the gray water and GAC with a calculated rate constant of $52.53 \text{ g}/\text{mg}\cdot\text{h}$. The chemical reactions between the organic compounds and the functional groups of GAC were the slowest compared to the physical adsorption or physisorption and the diffusion mechanisms.

3.2.3 Thermodynamics

Eq. (13) defines the free Gibbs energy, an important thermodynamic property for comprehending the spontaneity of the reaction between target molecules and GAC (Inyinbor, Adekola and Olatunji 2016)

Table 4 Thermodynamic properties of granulated activated carbon during adsorption.

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)
308.15	-6.88	100.79	-24.38
313.15	-5.31		
318.15	-3.84		

$$\Delta G^0 = -RT \ln K_c \quad (13)$$

$$K_c = \frac{C_{ads}}{C_e} \quad (14)$$

where, ΔG^0 is the change in free Gibb's energy and K_c is the ratio between the DOC concentration adsorbed by the GAC (C_{ads} , mg/L) and in the solution (C_e , mg/L) at equilibrium. The change in enthalpy (ΔH^0 , kJ/mol) and entropy (ΔS^0) were also calculated to determine the nature of DOC adsorption using GAC. The equation below describes the relationship between K_c , ΔH^0 and ΔS^0

$$\log K_c = \frac{\Delta H^0}{2.303R} - \frac{\Delta S^0}{2.303RT} \quad (15)$$

The equilibrium constant (K_c) was calculated after obtaining the data from the thermodynamic experiments. K_c was found to have exponentially increased below 35 °C and decreased above 35 °C. To understand this occurrence, thermodynamic properties of the DOC adsorption using GAC were determined as shown in Table 4. Since the ΔG^0 values were negative, the adsorption reaction can be concluded as spontaneous at any given temperature. However, ΔH^0 was different for low and high temperatures. Negative ΔH^0 was calculated from 25 °C to 35 °C while ΔH^0 was positive from 35 °C to 45 °C. In this regard, the adsorption process was exothermic for temperatures below 35 °C, but endothermic under higher temperatures.

3.3 Orbitrap mass spectrometry

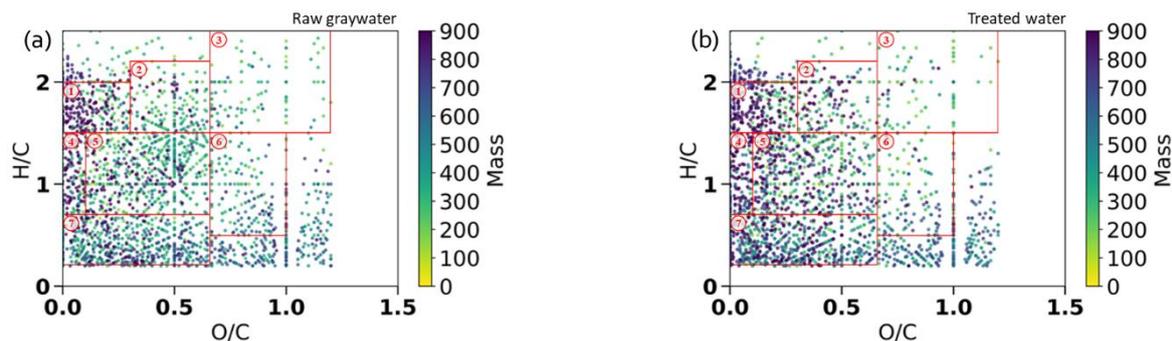
To further understand the organic matter present in UNIST graywater before and after adsorption, the orbitrap mass spectrometry (MS) was applied to perform an elemental analysis on the water samples. Fig. 4 shows the Van Krevelen diagrams that include the following characteristics of the organic compounds present in the water samples before and after the water treatment process: hydrogen to carbon (H/C) ratio, oxygen to carbon (O/C) ratio, double bond equivalent (DBE) and carbon (C) number. The Van Krevelen diagrams of Fig. 4a-b revealed the abundance of organic compounds for each classification in the raw graywater and treated water, respectively. In these plots, the O/C and H/C ratios of each formula were located along the x- and y-axis, respectively, to present the possible type of compounds that it is characterized with (Retelletti Brogi *et al.* 2018). The results show that most organic compounds in the graywater and treated water belong to (1) lipids, proteins, unsaturated hydrocarbons and lignin. It can also be observed in Fig. 4a-b that high

molecular weight (HMW) compounds are highly concentrated in the lipid area (1); however, Fig. 4b has a denser HMW formula count compared to Fig. 4a. Considering that overlapping of formulas is likely to occur in the Van Krevelen plots, it can be deduced that lipid-like substances with HMW formula remained in the water samples after the GAC has adsorbed the low molecular weight (LMW) compounds. This assumption is possible since molecular sizes of compounds can be directly proportional to their molecular weight. Based on the BJH pore analysis of GAC, the resulting average pore width (2.59 nm) can be smaller than the molecular size of HMW lipid- or fatty-like molecules which can either be elongated, spherical, or complex in structure (Tieleman, Marrink and Berendsen 1997). The other areas in the plots assigned to proteins (2), unsaturated hydrocarbons (4), lignin (5) and condensed aromatic carbons (7) may also have similar situations with the lipid group.

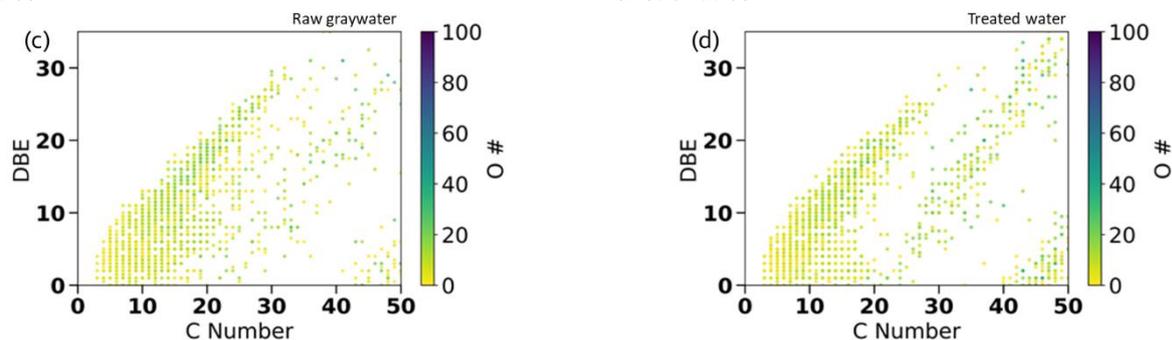
The formula of each type of organic compound that are grouped in Fig. 4a-b were also quantified. Fig. 5a shows the formula count of the organic compounds present in the raw graywater and treated water which were classified under the seven organic groups previously mentioned. The figure shows that the actual graywater has a significant number of condensed aromatic structures, followed by lignin-like, unsaturated hydrocarbons and tannin-like formulas.

This coincides with the FT-ICR-MS results of Maizel and Remucal (2017) who reported about the molecular compositions of several municipal wastewaters. They revealed that terrestrial-derived aquatic DOM are abundant in lignin- and tannin-like compounds with low aromaticity, which can be attributed to the high number of unsaturated hydrocarbons. This differentiates the actual graywater in this study by having a high number of formulas with condensed aromatic structures.

A significant decrease can be observed on the formula count of carbohydrates (from 117 to 80), proteins (from 194 to 132), lignin (from 506 to 325) and tannins (from 228 to 187). These changes are reflected in Fig. 5b wherein the light-colored points (green to yellow) that represent LMW formula have decreased in number which resulted to a denser plot of dark-colored points pertaining to HMW formula. On the other hand, a notable increase in the formula count of condensed aromatic structures and lipids and a negligible change in the unsaturated hydrocarbons were also observed. The apparent increase can be attributed to the possibility of the organic compound transformation occurring during and after the adsorption process. In this regard, it can be assumed that new formula emerged after getting in contact and reacting with the adsorbent. This phenomenon was also observed in other water treatment processes that involve physical, chemical and microbial reactions (Li, Kuppler and Zhou 2009, Twardowska, Schramm and Berg 2004). The complex matrix of the actual graywater can also be causing the noticeable increase of formula count. It has been reported in previous studies that matrix effects can interfere with the chemical analyses of MS equipment (Deng, Li, Yu and Zhang, 2016, Sanchís, Oliveira, de Leão, Farré and Barceló 2015). Sanchís *et al.* (2015) reported that the complexity of the matrix can



(a) Van Krevelen plot of raw graywater based on the H/C vs. O/C ratios (b) Van Krevelen plot of the treated water based on the H/C vs. O/C ratios



(c) DBE vs. C number of the molecular formulae in the raw graywater (d) DBE vs. C number of the molecular formulae in the treated water

Fig. 4 Van Krevelen plots of the water samples based on the H/C vs. O/C ratios and double-bond equivalent (DBE) vs. C number of the molecular formulae detected using the Orbitrap mass spectroscopy. H/C vs. O/C plots classified the organic molecules according to (1) lipids, (2) proteins, (3) carbohydrates, (4) unsaturated hydrocarbons, (5) lignin, (6) tannins and (7) condensed aromatic carbons

suppressed the signals of the analytical equipment, thereby lowering the number of detected formulae prior to wastewater treatment. In this case, the GAC adsorption greatly reduced the matrix effects by removing most of the organic contaminants. This enabled the detection of other compounds present in the actual graywater, specifically condensed aromatic structures and longer chains of unsaturated hydrocarbons. To summarize these results, it can be deduced that the lignin-like organic compounds in this graywater were more likely to be adsorbed using GAC.

Fig. 5b shows the double-bond equivalent and carbon number (DBE/C) ratio of the organic formula. This ratio measures the aromaticity of the formula present in the water samples wherein a value greater than 0.7 indicates a fused-ring structure (Hockaday, Grannas, Kim and Hatcher 2006). On the other hand, condensed tannin structures have DBE/C ratios of 0.6 while alkenes have lower values depending on their respective C number, a higher C number corresponds to a lower DBE/C ratio. Fig. 5b shows a high formula count of fused ring structures (DBE/C \geq 0.7) which accounted for more than 50% of the unique formula present in the graywater. A significant increase can be observed for DBE/C ratios around 0~0.1 (alkane and alkene structures) and 1.0~ (fused-ring structure) while the formula count for the other ratios decreased in general after adsorption. As previously mentioned, the increase can be attributed to the transformations of organic compounds after water treatment

while the decrease of the organic formula with DBE/C ratios from ~0.2 to ~1.0 was due to GAC adsorption. DBE/C ratios at the opposite ends of the plot indicates the presence of alkane (DBE/C = 0), alkene ($0 < \text{DBE/C} \leq 0.1$) and condensed aromatic structures (1.0~). These structures may either have larger structures compared to the GAC pores, have high molecular mass, or have transformed to a unique organic compound upon reacting with GAC and other compounds present in the water samples; hence, the increase in the formula count.

Elemental analysis of the organic compounds in the water samples was also performed to categorize the organic formula according to the following: CHO, CHON, CHOS and CHONS. These categories refer to the elements present in the formula which are carbon (C), hydrogen (H), oxygen (O), sulfur (S) and nitrogen (N). Fig. 5c shows the number of unique formulas in the raw graywater and treated water. This figure also reveals which category has the highest affinity to GAC during adsorption. CHON formulas gave the highest difference between the raw graywater and treated water with 166 formulas removed by GAC adsorption. This was followed by CHONS with 57 formulas, CHO with 34 and CHOS with 28. Based on these results, it can be assumed that the formula that carries nitrogen is more likely to be adsorbed while sulfur decreases that tendency. This assumption can be based on the high removal of lignin-like formulas, which are usually

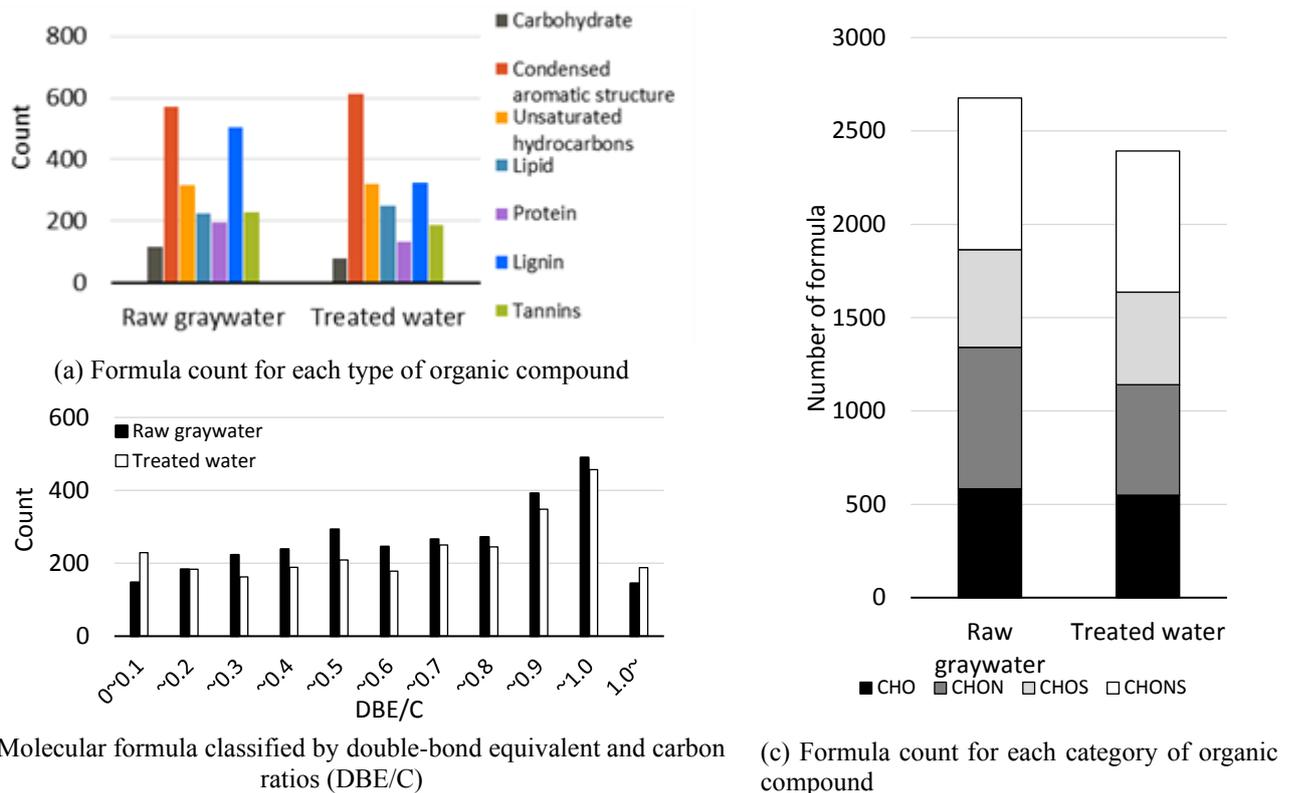


Fig. 5 Quantitative and molecular analyses of the organic compounds detected in the actual graywater and treated effluent.

associated with nitrogen-containing compounds (Maizel and Remucal 2017).

3.4 Effect of parameters

After the adsorption experiments, the results were recorded and analyzed. The water sample pH rose from an initial of 7 to around. On the other hand, the other parameters such as conductivity, DOC and TN were reduced since the organic matter and ionic substances in the graywater were adsorbed into GAC. The combination of increased pH and decreased conductivity due to GAC adsorption has been reported to be caused by the adsorption of metal complexes in a ligand-like manner (Wasay, Barrington and Tokunaga 1999).

3.4.1 Dosage

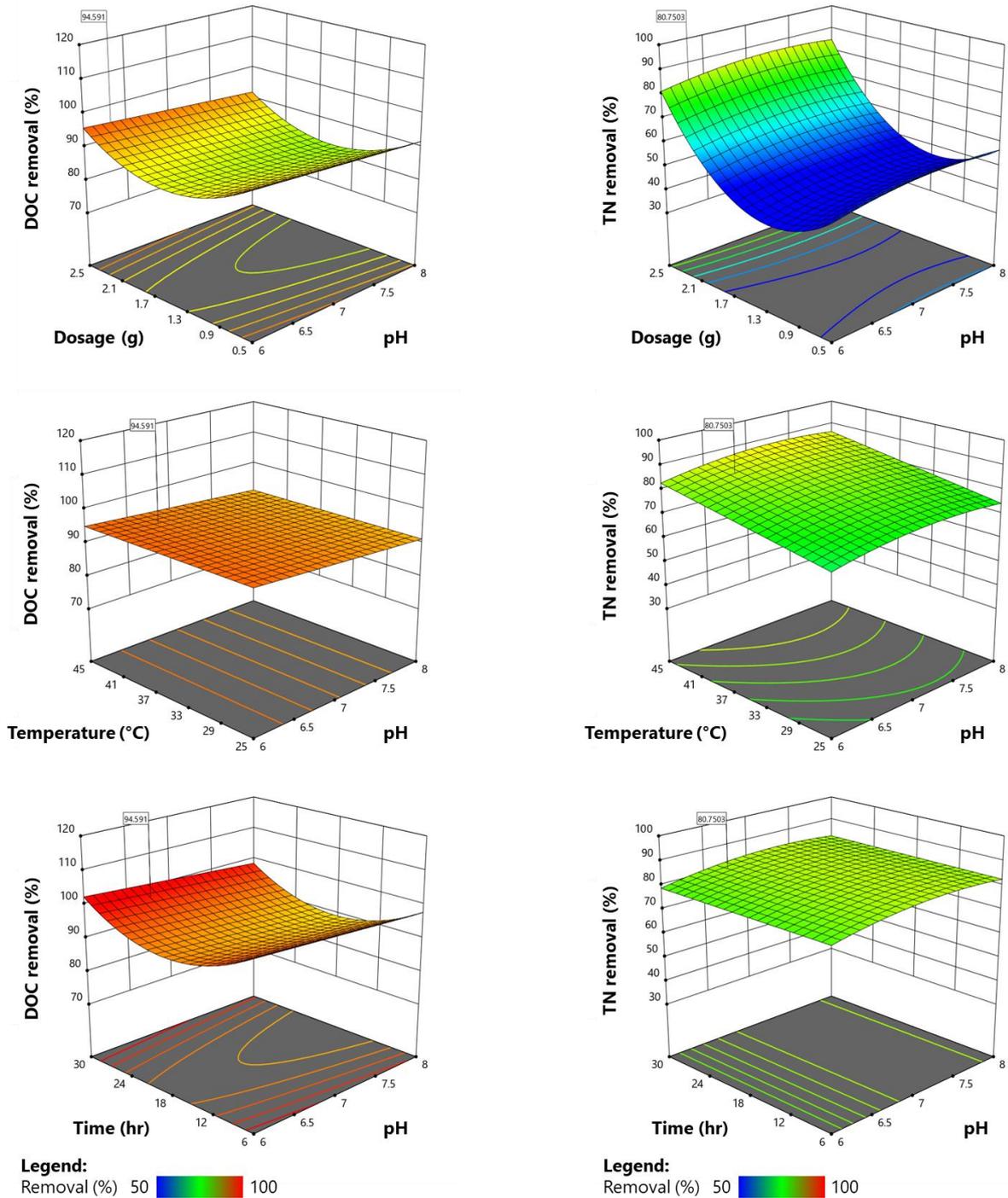
Fig. A1 shows the results of varying GAC dosage on the removal of organic matter in terms of DOC and TN concentrations. It can be observed in Fig. A1a that the removal percentage of both DOC and TN increased with increasing GAC. GAC was able to adsorb a maximum of 78.52% of DOC; however, the removal percentage between the dosages did not differ drastically. 0.1 g of GAC was also able to significantly remove DOC at 68.12% which indicate that the GAC has a high affinity towards organic matter as confirmed by previous studies (Cheng, Dastghei and Karanfil 2005, Gur-Reznik *et al.* 2008, Nguyen *et al.* 2012, Zietzschmann, Stützer and Jekel 2016). In contrast, TN has a lower removal percentage with only 0.39% at a GAC dosage of 0.1 g and a 26.48% maximum TN removal for less than 1.0 g of GAC. Though a notable difference was

observed between the minimum and maximum removal percentages, the remaining 17.28 mg/L of TN after the maximum removal was still higher than the water standard for recreational use (10 mg/L).

An observable trend for TN removal was also seen wherein the TN removal percentage increases as the dosage of GAC also increases. This implies that the dosage of adsorbent has a significant effect on TN removal. For the other water quality characteristics, the pH of the treated water after in contact with GAC during adsorption slightly increased compared to the initial pH of graywater at 7.1. However, it can be observed in Fig. S2a that there was no notable trend between the dosage and pH as the pH of the treated water for each dosage varied randomly from pH 7.6 to 8.0.

3.4.2 Contact time

Fig. A1b shows the effect of contact time to the removal of DOC and TN while the other parameters remain constant. During the first few hours, a rapid removal of DOC can be observed in the figure, which slowed down after reaching the fourth hour. The slowing down of the removal can be attributed to the saturation of active sites as the contact time between the target molecules and GAC increases. In this regard, the available active sites for DOC substances before the adsorption process started were rapidly filled until saturation was achieved. On the other hand, the TN was consistently removed within the range of 20.0% to 28.0%. This indicates that contact time does not affect the removal of TN from the graywater since it seemed that there was an instant reaction between TN compounds and GAC. After adsorption, the pH of



(a) Interaction between parameters and DOC removal

(b) Interaction between parameters and TN removal

Fig. 6 Three-dimensional parametric interaction using response surface methodology (RSM)

graywater also increased to approximately 8.0 while the conductivity decreased to around 400 $\mu\text{S}/\text{cm}$ after mixing as shown in Fig. S2b. The final DOC concentration in the remaining solution (24-hr contact time) was around 2.0 mg/L while TN has 20.15 mg/L, which is still beyond the water standard limits for recreational use.

3.4.3 Temperature

The effect of varying temperature on the adsorption of organic matter using GAC was also evaluated and shown in

Fig. A1c. As the temperature increased from 25°C to 35°C, the DOC removal also increased to a maximum of 93.62% at 35°C; however, it started decreasing as the temperature rose beyond 35°C. This could imply that the reactions between the organic matter and GAC are less likely to occur at higher temperatures. On the other hand, pH showed a higher increase in value as compared to the other adsorption experiments that yielded a pH range of 7.5 to 8.0. As the temperature rose to 45°C, the final pH of the solution also increased until it reached a maximum of 8.5 while the

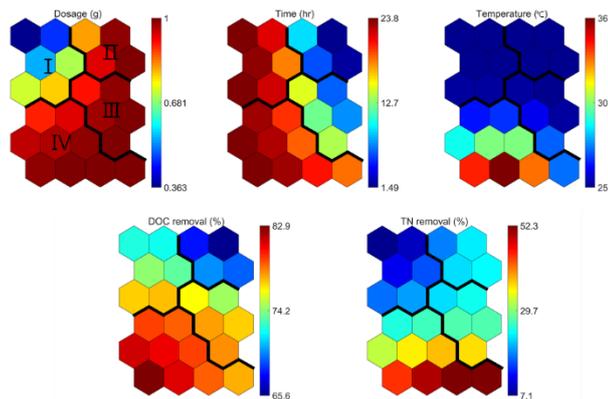


Fig. 7 SOM maps for GAC dosage (g), contact time (hr), temperature (°C), DOC removal (%) and TN removal (%)

conductivity showed a decreasing tendency. Previous parametric conditions for the adsorption experiments also produced treated water with higher pH which can be attributed to the ligand-like bonds of metal or ionic complexes in the water samples. In this regard, the much lower conductivities of the treated water after subjecting the samples to increasing temperatures can be assumed to be caused by the increasing amount of the ligand-like bonded complexes of ions and GAC (Wasay *et al.* 1999). This occurrence implies that more ionic complexes were adsorbed at higher temperatures. In this case, the increasing removal of ionic complexes could likely reduce the available active sites in GAC to attract pure organic matter hence the decreasing removal percentage of DOC at higher temperatures. In contrast, the removal percentage of TN increased until 74% as temperature rose, with final TN concentrations of below 20.0 mg/L. TN concentration was at its lowest under a higher temperature compared to the outcome of all parametric conditions. Under a 45 °C environment, the final TN concentration was reduced to 7.13 mg/L which was lower than the water standard for rivers. The results of this experiment revealed that temperature can be assumed as a significant factor for TN and DOC removal since both types of substances were sensitive to the changes in temperature.

3.5 Optimization studies

The MATLAB function “ccdesign” was applied to generate a total of 36 adsorption experimental runs using a five-level circumscribed central composite design (CCC). Four parameters were considered for the optimization experiments: pH, dosage of GAC, contact time and temperature. Using the Design Expert (version 11) software, it was found that the optimal conditions to obtain both maximum DOC and TN removal are to set the pH at 6.3 with 2.46 g of GAC for every 30 mL of graywater sample. The optimum contact time for the adsorption process is 23.39 hrs under 38.6 °C. These conditions can yield the predicted removal percentages of 94.59% and 80.75% for the DOC and TN, respectively.

Using the analysis of variance (ANOVA) for the reduced quadratic model, dosage is the most significant

parameter for the DOC and TN removal. Equations 16 and 17 below show the final equations in terms of actual factors that only considered the other significant terms

$$\begin{aligned} \text{TOC removal} = & 135.80 - 1.88\text{pH} - 2.19t \\ & - 27.63\text{dosage} + 0.06t^2 \\ & + 9.25\text{dosage}^2 \end{aligned} \quad (16)$$

$$\begin{aligned} \text{TN removal} = & -101.34 + 43.14\text{pH} + 0.59T \\ & - 53.21\text{dosage} - 2.95\text{pH}^2 \\ & + 22.40\text{dosage}^2 \end{aligned} \quad (17)$$

Three-dimensional plots of the interaction between parameters are shown in Fig. 6a for DOC removal and Fig. 6b for TN removal. In this figure, the dosage vs. pH plots for both DOC and TN removal showed significant curvatures which indicate the sensitivity of the response with respect to dosage.

To summarize the effect of three parameters, SOM was performed for the GAC dosage, contact time, temperature, DOC removal and TN removal. Fig. 7 shows the respective SOM maps with each map divided into four clusters. Cluster IV was characterized as high GAC dosage, long contact time and high temperature. This condition resulted in high DOC and TN removal, which also found in the cluster IV. On the other hand, cluster I was characterized with low GAC dosage and high contact time, while cluster II depicted the opposite condition. We found that TN removal was more affected by GAC dosage, while DOC removal was more influenced by contact time, based on their behavior in cluster I and II.

4. Conclusions

This study investigated the organic matter content of an actual graywater sample in terms of DOC and TN. The UNIST graywater was treated using adsorption to remove the organic contaminants. Using orbitrap MS, the organic matter content between an untreated graywater and the GAC-treated effluent were compared and yielded a significant formula count difference for the samples. It was revealed that CHON formula has the highest removal. The following results were also concluded from this study:

- Dosage was the most significant parameter for both DOC and TN removal while temperature also played a huge role in increasing the removal of TN.
- Results from the isotherm studies fit the Freundlich equation with an R^2 of 0.9705 indicating a heterogeneous GAC surface with a multilayer characteristic. Kinetics experiments fit the pseudo-second order equation with an R^2 of 0.9998 implying that chemisorption is the rate-determining step between the organic compounds and GAC at rate constant of 52.53 g/mg·h. Lastly, the reaction between GAC and organic compounds at low temperatures were found to be spontaneous and exothermic.
- For the optimization, the conditions were set to achieve a maximum DOC and TN removal. The optimum parameter values are the following: pH 6.3, 2.46 g of GAC

for every 30 mL of graywater sample, 23.39 hrs contact time and 38.6°C.

Acknowledgments

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