Extending granular activated carbon (GAC) bed life: A column study of *in-situ* chemical regeneration of pesticide loaded activated carbon for water treatment

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Abstract: *In-situ* chemical regeneration of granular activated carbon (GAC) may represent an advantageous alternative to conventional off-site thermal regeneration in water treatment applications. The performance of chemical regeneration of carbon exhausted by metaldehyde and isoproturon was investigated using rapid small-scale column tests, performed using a sequence of pesticide adsorption and chemical regeneration cycles with a novel alkaline-organic regenerant solution. A fresh regenerant solution was able to achieve 82% and 45% regeneration of carbon exhausted by metaldehyde and isoproturon, respectively. After the first regeneration the performance declined slightly to 79%, and to 36% after the fourth regeneration. A comparison using a thermally regenerated (operational) carbon suggested that chemical regeneration was more beneficial for carbon exhausted by metaldehyde. The regenerant solution has a potential to be re-used multiple times, thereby minimizing the amount of waste chemicals generated. A series of carbon characterization tests showed that chemical regeneration did not alter the surface area, pore size distribution and surface chemistry of the carbon. As part of the evaluation, the adsorption thermodynamics of virgin and chemically regenerated carbons were determined using isothermal titration calorimetry to evaluate the adsorption behaviour of the pesticides on the carbon samples. The relatively high regeneration efficiency achieved by chemical regeneration, and minimal deleterious effect to the physico-chemical properties of the carbon, demonstrated the beneficial potential of this process as an alternative to conventional thermal regeneration of GAC.

Keywords: *In-situ* chemical regeneration, pesticides, adsorption, activated carbon, water treatment.

1. Background

The presence of weakly adsorbable pesticides, e.g. metaldehyde, in raw water continues to challenge water treatment processes, and specifically granular activated carbon (GAC) filter beds, in achieving regulated drinking water quality standards. Metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetroxocane) is of particular concern in the UK (and was temporarily banned in 2018-19), owing to its poor removal during water treatment, typically caused by rapid exhaustion of GAC filters (Castle et al., 2017). The accelerated exhaustion leads to the need for frequent off-site thermal regeneration, which is the most commonly practiced carbon regeneration technique (UK Water Industry Research, 2017), resulting in a significant operational cost and an environmental (energy/CO_2) penalty. An alternative approach is to conduct the regeneration of the GAC by alternative chemical means. Chemical regeneration can be performed on-site, either *in-situ* or *ex-situ*, by exposing the spent (exhausted) GAC to a selected chemical, or combination of chemicals, to remove the adsorbed contaminants (Matheickal et al., 1998; Tamon et al., 1990). Previously, it was speculated that a partial chemical regeneration may prolong carbon life between thermal regeneration operations, or prior to disposal and carbon replacement (Kow et al., 2016). Additionally, chemical regeneration usually does not require high temperatures (Salvador et al., 2015) which may otherwise damage the porosity of the carbon.

A number of chemicals have been considered previously for chemical regeneration, but their reported performance has not been entirely satisfactory, mainly because of their limitation in removing certain types of contaminants (Larasati et al., 2021). Among these studies, it was reported that solvents with a high solubilizing power, such as ethanol (Matheickal et al., 1998), or an aggressive nature, such as sodium hydroxide (Sutikno and Himmelstein, 1983), were able to regenerate carbon exhausted by phenol. However, these chemicals, individually, have been shown to display a limited ability to remove other aromatic compounds, such as nitrobenzene (Leng and Pinto, 1996). Recently, we have reported batch tests that showed a mixture of alkali and alcohol, specifically 0.5 M sodium hydroxide in 80% (v/v) ethanol ($NaOH/CH_3CH_2OH$), achieved a high desorption efficiency of a range of organic contaminants adsorbed to GAC. This was attributed to the combination of adsorbed compound re-

dissolution and changes to the surface functional groups of the carbon, facilitating the desorption of relatively hydrophobic and hydrophilic contaminants (Larasati et al., 2020).

Most previous chemical regeneration studies have been conducted at laboratory scale using batch tests (Leng and Pinto, 1996; Martin and Ng, 1984), but to-date the performance of chemical regeneration in continuous column tests has not been widely investigated. It is important to understand the behaviour of the carbon during the adsorption and desorption phases under continuous flow conditions, which are expected to be markedly different to those in batch test conditions. Thus, column tests are more representative of the performance of adsorbents in granular media beds in practice (Patel, 2019), as indicated by the development and widespread use of rapid small-scale column tests (RSSCTs); these were employed in this study, as described subsequently.

The main aim of the present work was to investigate the performance of virgin, chemically and thermally regenerated carbon exhausted by selected 'target' pesticides in successive adsorption-regeneration column tests. The reusability of the $NaOH/CH_3CH_2OH$ regenerant solution was also evaluated, by comparison with fresh regenerant solutions. In addition, the impact of chemical regeneration on the physical and chemical properties of the carbon was determined, as in most previous studies, these have not been considered. As part of the evaluation of the chemical regeneration performance, the adsorption thermodynamics of virgin and chemically regenerated carbons for the selected compounds have been evaluated using isothermal titration calorimetry (ITC). The ITC method has been used widely to investigate interactions between molecules as it has the ability to accurately measure the Gibbs free energy ($\Delta_{ads}G$), enthalpy (heat of adsorption, $\Delta_{ads}H$) and entropy ($\Delta_{ads}S$) associated with these interactions (Lewis and Murphy, 2005). These thermodynamic parameters can provide valuable information regarding the surface characteristics of virgin and regenerated carbon, as well as the adsorption mechanisms of the target compounds (Tran et al., 2016).

2. Materials and Methods

A commercial GAC Filtrasorb 400 (F400) supplied by Chemviron Carbon (Chemviron Carbon, 2015) was used throughout the tests; this GAC type is commonly used in UK drinking water treatment

plants. Samples of a thermally regenerated F400 carbon were obtained from the Whitacre Water Treatment Works of Severn Trent Water, UK. The carbon is thermally regenerated approximately every two years and the samples obtained had been regenerated 3 times since 2013. In both cases, the carbon was initially washed using ultrapure reverse osmosis (RO) water until its pH was stable, dried to constant weight and stored in a desiccator prior to use in the tests. The target contaminants used in the tests were isoproturon (3-(4-Isopropylphenyl)-1,1-dimethylurea, Sigma-Aldrich) representing a hydrophobic pesticide, and metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetraoxocane, Acros Organics) representing a hydrophilic pesticide.

2.1. Column tests

The equations and mathematical models used to dimension the rapid small-scale column tests (RSSCTs) are described in Part 1, Supplementary Information file. The RSSCTs consisted of successive exhaustion and regeneration phases. The **exhaustion (adsorption) phase** was conducted with the flow passing vertically upwards (up-flow) through the column and fully-immersed GAC layer to avoid of any possible formation of air bubbles. Influent and effluent samples were taken periodically until the contaminant concentration in the effluent was almost identical to the influent ($C/C_0 \sim 1$). The **regeneration (desorption) phase** was conducted using 10 bed volumes (BV), or equal to 6.4 mL, of regenerant solution consisting of a mixture of 0.5 M sodium hydroxide in 80% ethanol ($NaOH/CH_3CH_2OH$). The mixture was circulated continuously through the column of exhausted carbon with a flowrate of 2.5 mL min^{-1} to prevent localized equilibrium effects which may occur if the flow is stationary, and where contaminants might concentrate near to the pores of the carbon. The regeneration lasted for 2 h, which provided an adequate time to reach the maximum desorption of the contaminants (Larasati et al., 2020). Once completed, the regenerated carbon was rinsed using a circulated 10 BV (6.4 mL) of 0.025 M H_2SO_4 for 15 min, followed by 300 BV (192 mL) of RO water to remove the remaining chemicals.

The extent of adsorption, q_{exp}, during the experiment was calculated using Eq. (1) as follows:

$$q_{exp} = \frac{C_t - C_0}{M_{SC}} \times V \quad (1)$$

111

112 - where C_t and C_0 are the contaminant concentrations (mg L^{-1}) in the effluent at time t and the influent
113 concentration, respectively, M_{sc} is the GAC mass, and V is the volume of water passed through the
114 column (L).

115 The data obtained from the RSSCTs were analysed using the Thomas model (Thomas, 1944),
116 a widely used model to describe adsorption phenomena in a column study (Patel, 2019), which assumes
117 that the adsorption occurs via a pseudo second-order reaction and is expressed as follows:

118

$$\frac{C_t}{C_0} = \frac{1}{1 + exp\left(\frac{k_{TH} q_0 m}{Q} - k_{TH} C_0 t\right)} \quad (2)$$

119

120 - where k_{TH} is the Thomas adsorption rate constant (L min^{-1} mg^{-1}), q_0 is the adsorption capacity of the
121 carbon (mg g^{-1}), m is the mass of the carbon inside of the column (mg), Q is the flowrate (mL min^{-1})
122 and t is the time (min). Another useful parameter in monitoring the adsorbent column performance is
123 the mass transfer zone (MTZ) as shown in Eq. (3).

124

$$MTZ = H(1 - \frac{q_b}{q_0}) \quad (3)$$

125 - where H is the column length (mm) and q_b is the extent of adsorption at the point of breakthrough
126 (mg g^{-1}). The length of the MTZ depends on the mass transfer rate, and efficient adsorption corresponds
127 to a short MTZ.

128 The performance of the regeneration was evaluated as the regeneration efficiency (RE), as
129 follows:

130

$$RE(\%) = \frac{q_2}{q_1} \times 100\% \quad (4)$$

- where RE is the ratio of the regenerated carbon adsorption capacity, q_2 (mg g^{-1}), to the initial carbon adsorption capacity, q_1 (mg g^{-1}), for a target contaminant.

2.1.1. Single target contaminant: Pesticides

Solutions of isoproturon and metaldehyde at 1 mg L^{-1} concentration were used as target contaminants. A concentrated stock solution of 20 mg L^{-1} of each contaminant was prepared in a buffered ultrapure RO water using 1 mM sodium bicarbonate ($NaHCO_3$), and with the pH of the solutions adjusted to 7.0 ± 0.1 using either 0.01 M HCl or 0.01 M NaOH. Subsequently, the concentrated solution was pumped to a mixing chamber, where it was dispersed with the experimental solution matrix. The concentration of the mixed solution was frequently monitored.

2.1.2. Comparison of chemical and thermal regeneration

The pre- and post-chemical regeneration adsorption performance of virgin carbon F400 (V-C) and thermally regenerated carbon F400 (TR-C) with solutions of the target pesticides were investigated using the RSSCT system. The pesticide solutions were either metaldehyde or isoproturon at 1 mg L^{-1} in tap water from the Roger Perry Laboratory, Imperial College London. Tap water was used in order to simulate real waters containing background organic matter (BOM). The tap water samples were initially de-chlorinated by leaving the water open to the air overnight, allowing the residual chlorine to decay and/or evaporate from the water (Table S2, Supplementary Information). The de-chlorination was necessary as the activated carbon has an ability to adsorb and/or react with chlorine (F. Meng et al., 2019), potentially affecting the adsorption of the target contaminants on the carbon.

2.2. Analytical methods

Isoproturon and metaldehyde concentrations in water samples were measured using Ultra/High-Performance Liquid Chromatography (UHPLC) with Quadrupole-Time of Flight (Q-TOF) mass spectrometry (Synapt G2-Si High Definition Mass Spectrometry, Waters Corp.) using an Electrospray ionization (ESI) technique in positive mode. An Acquity UPLC BEH C18 column (2.1 x 100 mm, 1.7

μm particle size, Waters Corp.) was used and maintained at 40 °C for the analysis. The mobile phases were, A: LC-MS grade water and 0.1% of formic acid (VWR), and B: LC-MS grade acetonitrile (Honeywell). The gradient program was as follows: 0 – 0.5 min isocratic of 30% B (v/v), 0.5 – 4 min linear from 30 – 80% B (v/v), 4 – 5 min isocratic of 80% B (v/v), 5 – 7 min linear from 80 – 30% B (v/v) and 7 – 10 isocratic of 30% B (v/v). The total analysis time was 10 min, the flowrate was 0.2 mL min^{-1} and the injection volume was 5 μl. Solid phase extraction (SPE) was carried out as a sample preparation using pre-made SPE cartridges (Waters Sep-Pak C18, 55 – 105 μm particle size) prior to injection. The instrument was set to detect metaldehyde ions in MS/MS mode with a retention time of 2.45 and 3.75 min, respectively. For metaldehyde, the mass spectra of $[M+Na]^+$ (199 m/z) was obtained as the precursor ion and the most abundant product ion of 67 m/z was used for quantification. For isoproturon, the mass spectra of $[M+H]^+$ (207.3 m/z) was obtained as the precursor ion and the most abundant product ion of 72 m/z was used for quantification. Additionally, no internal standard was used, but leucine enkephalin solution at 20 pg nL^{-1} (Waters Ltd.), prepared in 50:50 (v/v) acetonitrile/LC-MS grade water and 0.1% of formic acid, with mass of 556.27 m/z was used as a reference mass using LockSpray automatic option in the mass spectrometry. The calibration range for both target contaminants was 5 – 1000 ng mL^{-1}.

The BOM in the tap water and test solutions was expressed as dissolved organic carbon (DOC), which was measured as non-purgeable organic carbon (NPOC) using a Shimadzu TOC V-WS instrument employing the UV/persulphate oxidation method.

2.3. Heat of adsorption of virgin carbon and chemically regenerated carbon

Thermodynamic properties relating to the adsorption of contaminants were determined using a VP ITC calorimeter (Microcal, Inc). In this study, the heat exchanged between the carbon and each target contaminant, isoproturon and metaldehyde, at 0.25 mM, was measured at 298.15 K (25 °C) to determine the thermodynamic parameters of the adsorption process. The adsorbents were a well-dispersed suspension of the virgin F400 and the chemically regenerated F400 carbon, both immersed in water for > 24 h at a concentration of 2 g L^{-1}. The test procedure was based on previous studies of

the adsorption of metals and methylene blue on carbon materials (Karlsen et al., 2010; Ortega et al., 2017).

The ITC data were automatically analysed using the Microcal Origin 7.0 software based on the binding isotherms (Figure S2 and S3, Supplementary Information). All the data were blank corrected for the heat of dilution of the target contaminant and water and the heat of interactions between carbon and water. The thermodynamic parameters, such as K_a (binding constant) and $\Delta_{ads}H$, were predicted as adjustable parameters in the fitting procedures of the Origin 7.0 software. Data were fitted using a non-linear least-squares algorithm (Levenberg-Marquardt algorithm). The adsorption $\Delta_{ads}G$ and $\Delta_{ads}S$ were calculated using Eq. (5) as shown below, where R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature of the measurement (K).

$$\Delta_{ads}G = -RT \ln K_a = \Delta_{ads}H - T\Delta_{ads}S \quad (5)$$

2.4. Carbon characterisation

To identify any deleterious effects on the carbon because of the application of the regenerant solution, key physical and chemical properties of the carbon were investigated. Prior to their analysis, samples of virgin GAC F400 were contacted with RO water or the $NaOH/CH_3CH_2OH$ mixture for 2 h, and then re-conditioned using H_2SO_4 and RO water to neutral pH. The regeneration and conditioning processes were repeated 10 times.

The surface area of carbon can be determined from nitrogen (N_2) adsorption-desorption isotherm data. The N_2 adsorption and desorption isotherms were measured using an automatic Quantachrome Autosorb iQ3 instrument. Prior to measurement, 100 mg of activated carbon samples were degassed at 280 °C for 12 h to remove any moisture present in the samples. The surface area and pore volume of the carbon samples were determined using Quantachrome Data Reduction software, which utilizes the Brunauer–Emmett–Teller (BET) and the Non-Local Density Functional Theory (NLDFT) approach based on a slit-shaped pore equilibrium model.

A standardized Boehm titration was performed to identify the potential changes to the surface functional groups of the carbon caused by the chemical regeneration. The standardized procedures of the test followed those reported by Goertzen et al. (2009) and Oickle et al. (2010).

To identify the changes in the chemical composition of the carbon, an elemental analysis for C, H, N, S and O was performed by MEDAC Ltd. (Surrey, UK). Additionally, a sodium (Na) analysis was carried out to investigate the presence of any remaining regenerant solution on the regenerated carbon. A 0.5 mg quantity of carbon was allowed to stand for 4 h in an acid solution prepared using 1 mL of RO water, 2 mL of concentrated HNO_3 and 6 mL of concentrated HCl. Prior to analysis using ICP-OES (Avio 500, PerkinElmer, USA), the acid solutions were diluted 5 times in RO water, and filtered by 0.45 µm cellulose nitrate membrane (GE Whatman).

3. Results and Discussion

3.1. Breakthrough curve of pesticides

The breakthrough curves of metaldehyde and isoproturon in successive adsorption-regeneration cycles are presented in **Figure 1**. To reach the full breakthrough ($C/C_0 \sim 1$) using a virgin carbon, at a relatively high influent concentration of 1 mg L^{-1} of pesticides, 56000 BV and 100000 BV were required for metaldehyde and isoproturon, respectively, showing that the isoproturon uptake was almost double that for metaldehyde. The results indicated a greater affinity of the carbon for isoproturon than metaldehyde because isoproturon is more hydrophobic (log k_{ow} of 2.5) in character compared to metaldehyde (log k_{ow} of 0.12). The relatively high initial concentration of pesticides (1 mg L^{-1}) was selected in order to achieve a rapid carbon saturation, so that the performance of multiple regeneration cycles could be evaluated in a practical timescale.

For the tests using fresh regenerant, the regeneration efficiency (RE) for metaldehyde was relatively stable over a number of regeneration cycles at 76.4 – 82.3%, while the RE for isoproturon decreased slightly over successive cycles from 45.3% to 36.4%, by the fourth cycle, as shown in **Table 1**. As a comparison, San Miguel et al. (2002) reported that the RE achieved by a thermally regenerated F400 carbon using steam at 800 °C, or nitrogen at 650 – 1200 °C, was around 57 – 66%, with phenol

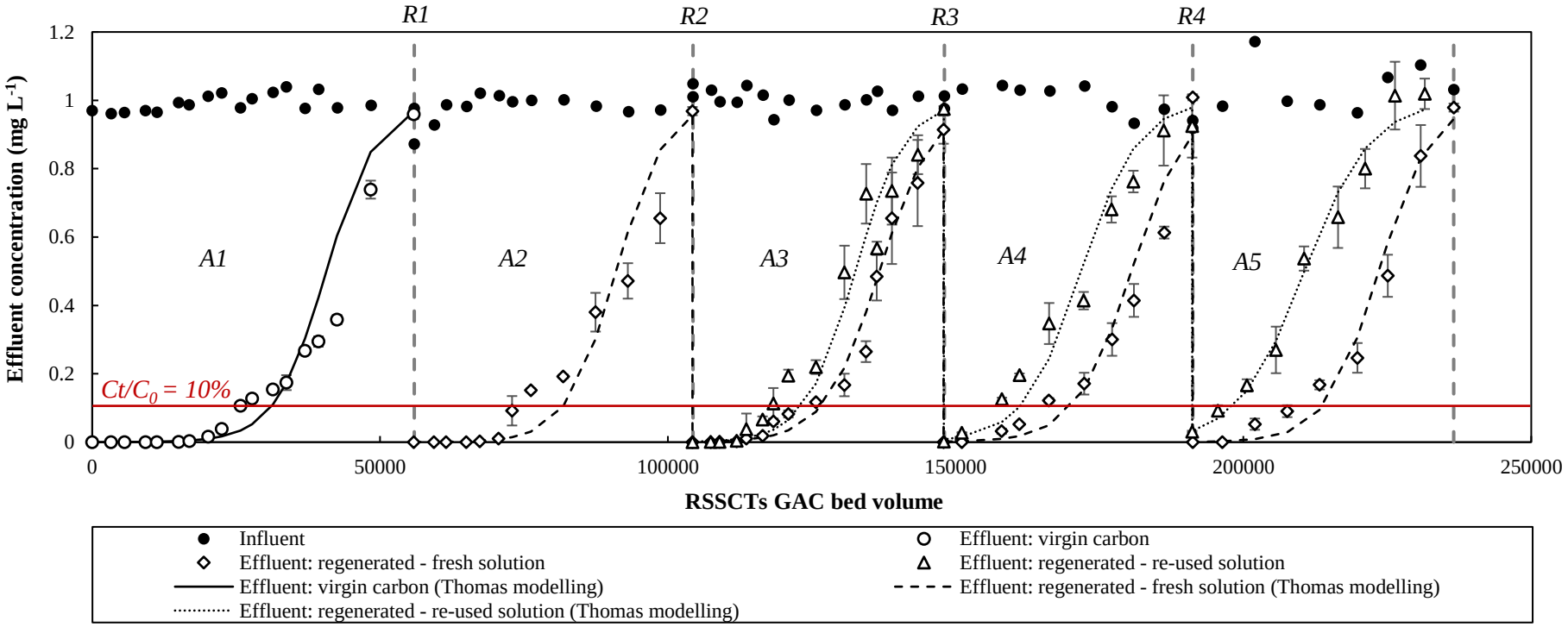
as the contaminant of interest. These preliminary results showing the higher REs that were achieved by chemical regeneration compared to thermal regeneration, highlight the potential advantage of the former in its application to full-scale GAC filter beds.

The re-used regenerant solution, in comparison to the fresh regenerant, exhibited lower REs. For metaldehyde, the RE decreased from 63.8% to 47.0% for the second (R2) and fourth (R4) regenerations, respectively, and for isoproturon, the RE decreased from 36.1% and 29.4% for the second (R2) and fourth (R4) regenerations, respectively. The decrease of RE, which declined further with the number of regeneration cycles for both target contaminants, was due to the accumulation of the desorbed compounds in the regenerant solution and these compounds which decrease the concentration gradient, affecting the desorption rate and diffusion. Nevertheless, the results of four regeneration cycles showed the feasibility of applying re-used regenerant solution. A recent study showed that alcohol (i.e. methanol) was able to be re-used also at least 4 times for carbon exhausted by PFOS (perfluorinated compounds) (P. Meng et al., 2019). This would minimize the volume of waste chemicals generated and thus the costs related to the fresh chemical procurement and ultimate waste disposal, thereby making chemical regeneration a potentially economically attractive alternative to thermal regeneration.

The prediction of adsorption capacity of the carbon using the Thomas model (Eq. 2) showed a relatively good agreement with the experimental data (**Table 1**), as indicated by the correlation coefficients (R^2) that were in the range of 0.87 – 0.97. The prediction was done in order to investigate whether the experimental results can be compared to existing theory. There was no clear pattern observed for k_{TH} values from multiple cycles of adsorption because the main parameters that strongly influence the k_{TH} values are the flowrate and the initial concentration of the contaminants (Patel, 2019), which were controlled to be relatively similar within 1%, throughout the experiment. It is noted that there was a marked difference in the values of q_0 and k_{TH} between isoproturon and metaldehyde. The k_{TH} values in this study are inversely correlated to the solid phase concentration or the adsorption capacity of the carbon and this phenomena was also reported elsewhere (Sankararamakrishnan et al., 2008). The greater k_{TH} and smaller q_0 values of metaldehyde compared to isoproturon showed that the

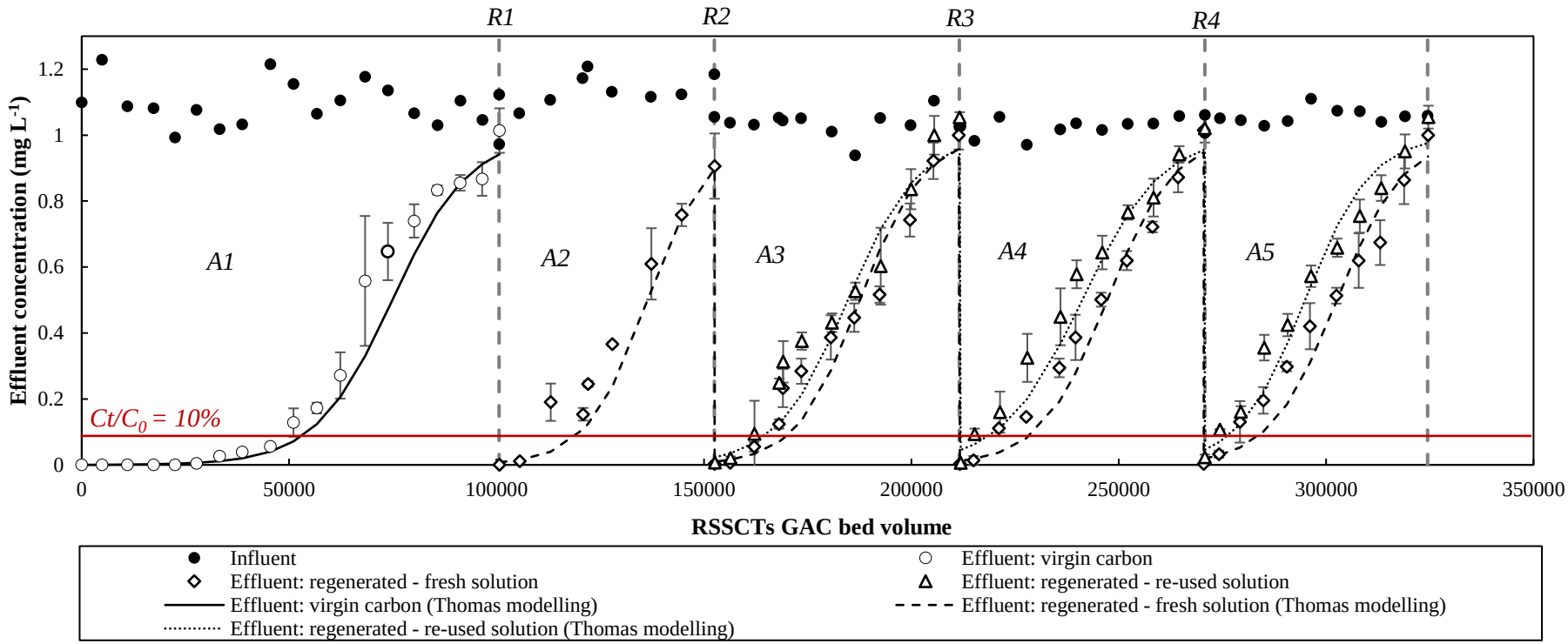
carbon saturated more rapidly with metaldehyde than with isoproturon, which is consistent with the reported behaviour of metaldehyde.

In comparing the data to the Thomas model, the analysis only considers the experimental values of the C_t/C_0 ratio that are greater than 0 (Aksu and Gönen, 2004). The model does not consider the phenomena at the initial stage of the adsorption where C_t is equal to 0, or when the pesticides are not yet detected in the effluent. The breakthrough point is commonly taken to be the time at which the effluent concentration is greater than the maximum permitted or otherwise defined. For comparison purposes, C_t/C_0 = 10% was considered as the breakthrough point in this study. **Figure 1** shows that for metaldehyde, the time required to reach the breakthrough was generally shorter compared to isoproturon for the first adsorption cycle. The performance of the carbon regenerated using fresh, followed with re-used, regenerant solutions demonstrated that the time to reach breakthrough was extremely short and barely existed after the 3rd cycle of regeneration for metaldehyde and after 2nd cycle for isoproturon. The rapidity of the contaminant adsorption at the initial stage of adsorption of each cycle declined due to the decreasing quantity of available adsorption sites (Patel, 2019).


R1
R2
R3
R4
A1
A2
A3
A4
A5
Ct/C0 = 10%
Effluent concentration (mg L-1)
RSSCTs GAC bed volume
0
0.2
0.4
0.6
0.8
1
1.2
0
50000
100000
150000
200000
250000
Influent
Effluent: virgin carbon
Effluent: regenerated - fresh solution
Effluent: regenerated - re-used solution
Effluent: virgin carbon (Thomas modelling)
Effluent: regenerated - fresh solution (Thomas modelling)
Effluent: regenerated - re-used solution (Thomas modelling)

280

281 (a)



(b)

Figure 1. Breakthrough curves for multiple cycles of adsorption (A1 – A5) and regeneration (R1 – R4) of the carbon exhausted by (a) Metaldehyde and (b) Isoproturon using 10 BV of regenerant solution (n= 4 for each point in A1 – A2, n = 2 for each point in A3 – A5).

Table 1. Thomas model parameters (q_0 and k_{TH}) and regeneration efficiency (RE) for adsorption-regeneration cycles using 10 BV of regenerant solution (n = 4 for virgin carbon, n = 2 for regenerated carbon).

Adsorption cycle		Metaldehyde				Isoproturon			
		q_{exp}	Thomas model		RE (%)	q_{exp}	Thomas model		RE (%)
			q_0	k_{TH}			q_0	k_{TH}	
1 – V-C		74.1 ± 1.4	76.8	0.87	-	153.6 ± 4.9	152.3	0.42	-
2 – CR-C	FR	60.9 ± 1.5	66.4	0.91	82.3 ± 3.6	69.6 ± 1.4	67.3	0.69	45.3 ± 0.9
3 – CR-C	FR	56.9 ± 2.3	61.2	0.67	76.7 ± 2.1	62.0 ± 0.9	66.1	0.51	39.5 ± 1.2
	RR	47.2 ± 0.5	53.3	0.72	63.8 ± 2.6	54.2 ± 3.4	60.2	0.46	36.1 ± 1.3
4 – CR-C	RR	56.6 ± 1.3	61.5	0.73	76.4 ± 0.8	60.3 ± 0.9	66.8	0.54	38.4 ± 0.0
	RR	41.2 ± 1.8	45.3	0.70	55.6 ± 0.7	46.9 ± 2.4	54.9	0.45	32.3 ± 0.5
5 – CR-C	FR	57.7 ± 0.9	60.9	0.86	77.9 ± 0.2	57.2 ± 1.8	61.5	0.48	36.4 ± 1.7
	RR	34.8 ± 3.2	41.6	0.60	47.0 ± 5.8	45.3 ± 0.3	46.4	0.49	29.4 ± 0.2

Notes: V-C is virgin carbon; CR-C is chemically regenerated carbon; FR is fresh regenerant; and RR is re-used regenerant; Units: q_{exp} and q_0 (mg g^{-1}); k_{TH} (mL min^{-1} mg^{-1}); and RE (%).

In principle, when the breakthrough point is reached, which is indicative of the mass transfer zone (MTZ), most of the bed capacity can be considered as fully used. Thus, a shorter MTZ is indicated by a narrower curve showing that the breakthrough is steep, while a longer MTZ corresponds to a broader curve showing that the adsorption process is less effective (Naja and Volesky, 2006). A comparison of the MTZ values is given in **Figure 2**, which indicated that for the 1st adsorption cycle (A1), the MTZ for isoproturon was shorter than for metaldehyde. However, for subsequent adsorption cycles with fresh regenerant, the MTZs for isoproturon were greater than for metaldehyde and increased with the number of the adsorption-regeneration cycles, indicating a faster carbon saturation. For metaldehyde, the MTZ was relatively stable over the sequence of cycles, with only a small increase. The changes in the MTZ correlate to the carbon adsorption capacity at each cycle as shown in **Table 1**. Compared to the results with fresh regenerant, the MTZ value was found to increase with re-used regenerant, for both metaldehyde and isoproturon, and the RE decreased with the number of the

adsorption-regeneration cycles. A greater MTZ value indicates a greater external and internal mass transfer resistance, most likely caused by the increasing retention of previously adsorbed contaminants. A previous study demonstrated that a carbon preloaded with contaminants had a greater diffusion resistance compared to a virgin carbon (Yu et al., 2009). A similar behaviour was shown in this study, where the greater accumulation of adsorbed contaminants by the carbon, the greater the MTZ value yielded and the greater mass transfer resistance.

The desorption of the target contaminants by the application of the $NaOH/CH_3CH_2OH$ regenerant provided readily available adsorption sites for subsequent adsorption as shown by the magnitude of RE achieved (**Table 1**). The regeneration performance also reflected a greater affinity of the target contaminants for the regenerant solution in comparison to the carbon. Furthermore, the changes in the surface chemistry of the carbon which weaken the interactions between the carbon and the contaminants aided the desorption (Leng and Pinto, 1996). However, the $NaOH/CH_3CH_2OH$ solution was not able to fully regenerate the exhausted carbon resulting in the presence of residual, irremovable quantities of metaldehyde or isoproturon on the carbon.

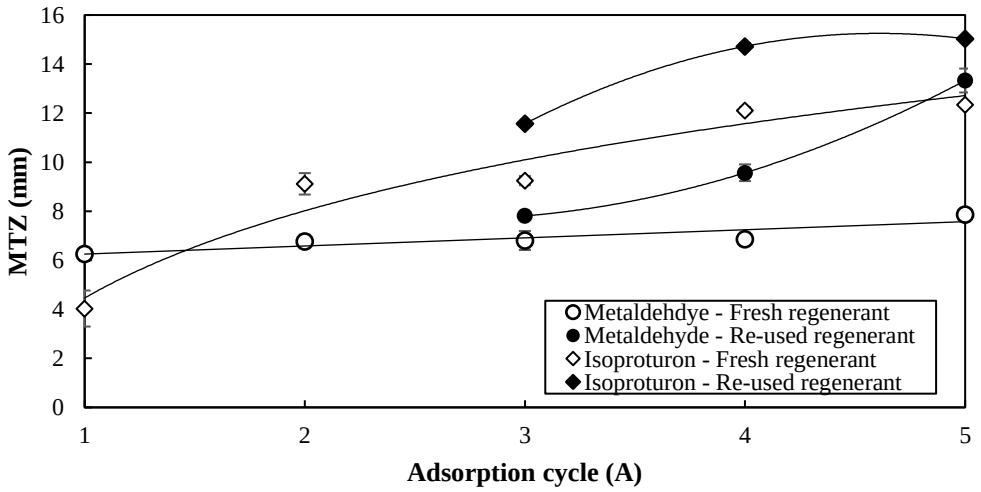
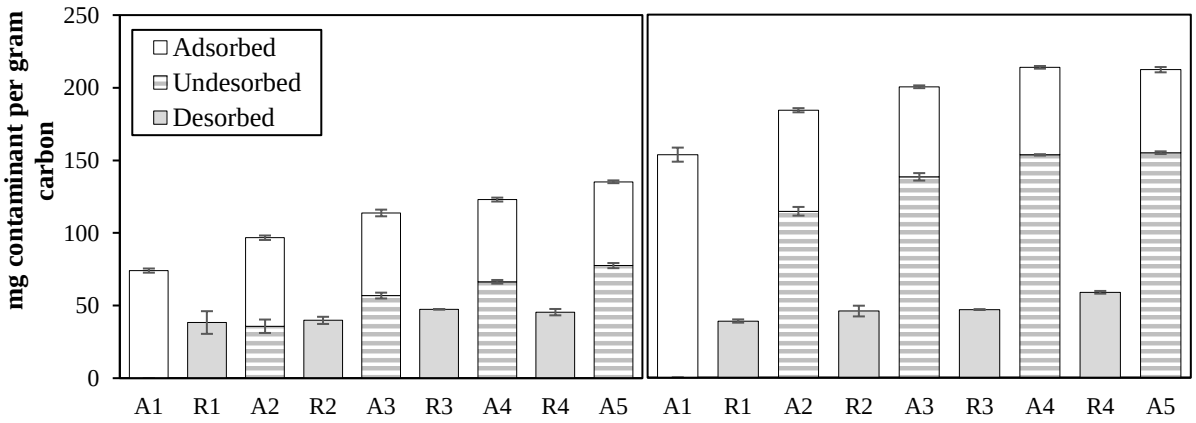


Figure 2. Variation of the MTZ with the sequence of adsorption cycles (A) for the target pesticides and type of regenerant (n = 2).

As summarized in **Figure 3**, the quantity of target contaminants desorbed using fresh regenerant at each regeneration cycle (R1 – R4) was relatively constant and these values correlated to the

reversibility of the adsorption process on the carbon. The mass of the adsorbed contaminant remaining on the carbon after regeneration (expressed as mg g^{-1} of adsorbent and calculated as the amount of contaminant adsorbed subtracted by the amount of contaminant desorbed), gradually increased with the number of adsorption and regeneration cycles, particularly for metaldehyde. When adsorbed to the carbon, the metaldehyde may degrade at the acidic sites of the carbon (Busquets et al., 2014), thus releasing sites and increasing the metaldehyde uptake in the subsequent adsorption step. Migration of the adsorbed contaminants between different sites or deeper into the carbon pores, thereby releasing accessible surface adsorption sites, may also account for the observed apparent increase in adsorption capacity. The accumulation of un-desorbed contaminants reflects the difficulty in removing the contaminant from the carbon pores and the strength of the interactions between the contaminant and the carbon through chemisorption.



(a) (b)

Figure 3. Quantity of target contaminant associated with the solid phase after the adsorption cycles (A1 – A5), and in the liquid phase after the regeneration cycles, using fresh regenerant (R1 – R4): (a) Metaldehyde and (b) Isoproturon (n = 2).

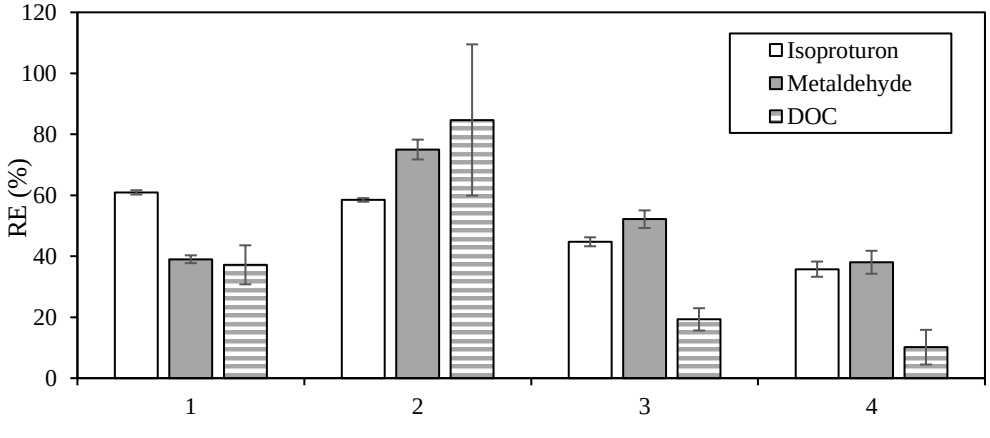
3.2. Comparison of chemical and thermal regeneration

As shown in **Figure 4**, thermal regeneration (TR-C) yielded REs for metaldehyde, isoproturon and background organic matter (DOC) of 39%, 61% and 37%, respectively. In comparison, the V-C after the first chemical regeneration had REs for metaldehyde, isoproturon and DOC of 75%, 59% and

85%, respectively. Thus, the results show that the chemical regeneration exhibited higher REs compared to thermal regeneration for metaldehyde and DOC, and an almost equal RE value for isoproturon. However, the TR-C sample tested had been previously regenerated more than 3 times, which may account for the apparent loss of its adsorption ability. In order to compensate for this, a comparison can be made between the TR-C results and those of the V-C that was chemically regenerated 4 times, as summarized in **Figure 4**. The REs for the chemically regenerated V-C (4^{th} cycle – using fresh regenerant) for metaldehyde, isoproturon and DOC were 52%, 44% and 25%, respectively. Compared to the TR-C, these REs were observed to be lower for isoproturon and DOC. Nevertheless, even after four cycles, the chemical regeneration exhibited a higher RE for metaldehyde compared to thermal regeneration. It should be noted that in practice there is typically a 10% top up of virgin carbon after each thermal regeneration (UK Water Industry Research, 2017), due to losses during transport and reactivation and to adjust the adsorption capacity of the carbon based on parameters such as iodine number. The virgin carbon top up may compensate for the loss of TR-C adsorption performance after multiple regenerations. Consistent with our previous findings, even though there was a decrease in the RE for isoproturon and DOC with the repeated use of the regenerant solution, the re-used solution nevertheless performed well for metaldehyde, as the contaminant of interest, and the RE yielded was similar to the RE of thermal regeneration. There was a dramatic decrease of RE for DOM after four cycles of regeneration, suggesting that the current chemical regeneration was not able to restore carbon capacity based on the DOM parameter; in these experiments the DOM was represented by the residual organic matter in tap-water following conventional water treatment processes.

It was apparent that TR-C had limited adsorption capacity for metaldehyde. TR-C differs to V-C in terms of its physical properties (surface area and pore volume) and surface chemistry (pH_{pzc}) (Table S3, Supplementary Information). It is well known that most micropollutants adsorb in the narrower micropores of activated carbon (Masson et al., 2016; Perry et al., 2005; San Miguel et al., 2001), making the presence of carbon micropores a crucial property of the carbon. The results showed that TR-C had lower values of micropore surface area and pore volume compared to V-C, thus resulting in a correspondingly lower adsorption of the contaminants.

The TR-C surface was more basic in nature compared to the V-C as shown in Table S3, Supplementary Information. Busquets et al. (2014) found that metaldehyde adsorption was not favoured in the presence of negatively charged functional groups. However, all of the experiments in this study were carried out at neutral pH, 7.0 $\pm$ 0.1 (pH below the carbon pH_{pzc}), suggesting that both carbon samples were predominantly positively charged (via protonated carboxylic acid and basic functional groups). Therefore, the basicity of the carbon may not be the main reason for the different uptake of metaldehyde on the TR-C and the V-C. However, the TR-C contained less phenolic and carbonyl surface functional groups compared to the V-C. These groups are known to affect the adsorption of organic compounds onto carbon (Stavropoulos et al., 2008). Previously, both a theoretical study (Ferino-Perez et al., 2019) and a laboratory investigation (Tao and Fletcher, 2013) suggested that metaldehyde adsorption involves hydrogen bonding with carbon surface functional groups, with or without mediation by water molecules. Thus, the reduced availability of these functional groups for metaldehyde to interact with, resulted in a lower capacity of the carbon for metaldehyde.



Notes:

1 Thermal regeneration
2 Chemical regeneration (1st cycle - fresh regenerant)
3 Chemical regeneration (4th cycle - fresh regenerant)
4 Chemical regeneration (4th cycle - re-used regenerant)

Figure 4. Regeneration efficiencies of the thermally regenerated and chemically regenerated carbon samples (n = 2).

The comparison shows that chemical regeneration was more beneficial than thermal regeneration for the carbon exhausted by metaldehyde, which is commonly the cause of an early GAC bed exhaustion (Castle et al., 2017). Additionally, thermal regeneration changed the surface chemistry of the carbon (Table S3, Supplementary Information), potentially decreasing its adsorption ability for metaldehyde. At some point, in a similar way to thermal regeneration, the carbon that was regenerated chemically, multiple times, will lose its ability to be used, ending the service life of the carbon bed. In this situation, rather than thermally regenerating the carbon, a full replacement of the carbon may be more appropriate (necessary). However, this may be disadvantageous in terms of having to landfill the spent GAC and an increased cost.

3.3. Heat of adsorption of virgin carbon and chemically regenerated carbon

The thermodynamic parameters corresponding to the adsorption of the target contaminants on virgin and chemically regenerated carbon were determined and the results are shown in **Figure 5**. The data fitting showed that both contaminants bind to two surface sites on the carbons, site 1 and site 2, and these binding sites might be interdependent, based on a sequential binding sites model (thermodynamic parameters and binding constants are presented in Table S4, Supplementary Information). For both carbon samples, at site 1, which is a relatively weak binding site ($\Delta_{ads}G$ for isoproturon and metaldehyde was in a range of -17.9 to -14.9 and -19.6 to -13.1, respectively), the values of all of the thermodynamic parameters were negative, indicating that the adsorption at this site was spontaneous and thermodynamically favourable ($\Delta_{ads}G < 0$) (Ferreira et al., 2017). This site might be where the target contaminants physically adsorb onto the carbon through electrostatic interactions, or involving van der Waals forces, or where the contaminants hydrated by water molecules interact with the hydrophilic sites on the carbon surface (Bansal and Goyal, 2005). The site 2 is a stronger binding site than site 1, with $\Delta_{ads}G$ for isoproturon and metaldehyde in a range of -34.6 to -32.7 and -36.5 to -32.2, respectively). The positive value of the $T\Delta_{ads}S$ for site 2 implies an involvement of dissociative mechanisms (Tran et al., 2016). There were complex interactions between the carbon and the target contaminants evident at this binding site. This site can be where a dynamic equilibrium occurred. The

positive entropy values in site 2 suggest that the contaminant molecules on the carbon surface adsorbed in a multilayer arrangement, where the molecules that are furthest from the carbon surface, or that have lower adsorption potential energy, become less stable and may be constantly desorbing and re-adsorbing, hence showing increasing disorder, and thus greater entropy. The formation of multilayers is expected before the contaminants fill the higher energy adsorption sites (high $\Delta_{ads}H$ or low $-\Delta_{ads}H$). Taking into account that the $\Delta_{ads}H$ values of isoproturon and metaldehyde exceeded 100 kJ mol^{-1}, and the process was endothermic at site 2, the adsorption mechanisms of isoproturon and metaldehyde most likely involved chemisorption-like interactions (Bansal and Goyal, 2005) and/or the contribution of hydrogen bonds (Tong et al., 2019).

The $\Delta_{ads}G$ values of regenerated carbon were more negative compared to virgin carbon, indicating that the adsorption of the contaminants on the regenerated carbon occurred mainly at the carbon surface and was not dominated by diffusion into deeper and smaller pores (Cestari et al., 2007). This was most probably because these pores were occupied by pre-adsorbed contaminant molecules that were not removed during the chemical regeneration process. The contaminants that interact with high energy sites of the carbon are usually strongly bound (Berger and Bhown, 2011) and are difficult to desorb during the regeneration process. The less negative $\Delta_{ads}H$ values for site 1, and less positive for site 2, of the regenerated carbon compared to virgin carbon, suggested that the adsorption process on the regenerated carbon involved a lower level of energy exchange. The lower energy sites became available for adsorption on the regenerated carbon because the contaminants were more readily desorbed from these locations during the regeneration. The decrease of $\Delta_{ads}H$ is also commonly associated with the increase of adsorbent surface coverage (Saha and Chowdhury, 2011), indicating the presence of previously adsorbed contaminants on the regenerated carbon.

Compared with virgin carbon, the entropy ($T\Delta_{ads}S$) values of the system when using regenerated carbon were less negative for site 1 and decreased for site 2 for both contaminants, indicating less interaction intensity between the contaminants and the carbon (Saha and Chowdhury, 2011), which corresponded to a lower adsorption capacity of the target contaminants by the regenerated carbon (**Table 1**).

For both target contaminants, the ratio of the enthalpy of the regenerated and virgin carbon for binding site 1 was in good agreement with the regeneration efficiency (RE) value obtained using the RSSCTs in the first cycle using fresh regenerant. This finding further suggested that the adsorption uptake of the target contaminant on the regenerated carbon mostly involved the interactions in binding site 1, a weaker binding adsorption site.

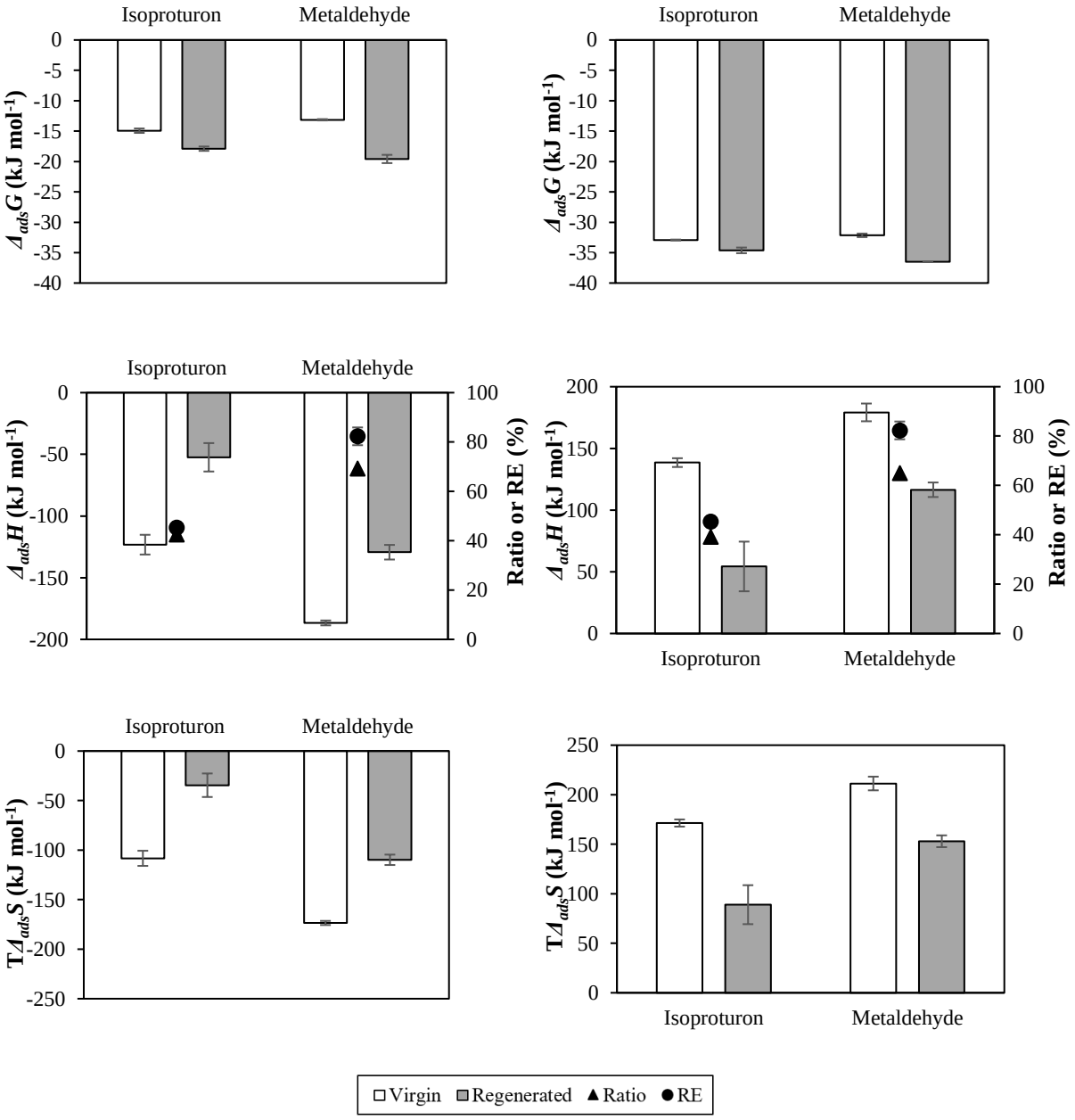


Figure 5. Thermodynamic parameters for compound adsorption by virgin and chemically regenerated carbon at binding sites 1 (a) and 2 (b) (n = 2).

3.4. Carbon characterisation

The data shown in **Table 2** summarizes the physical and chemical properties of the carbon that had been exposed to RO water (carbon + RO water) and the $NaOH/CH_3CH_2OH$ regenerant (carbon + $NaOH/CH_3CH_2OH$) ten times. Statistically, there were no significant differences in their physical (the BET surface area, micropore and macropore surface area and pore volume and average pore diameter) and chemical properties (surface oxygen functional groups and elemental composition) between the carbon samples ($p>0.05$). However, within the experimental error ($p<0.05$), there were some changes evident in the carbon mesopore surface area and pore volume. The possible reason for these is that a small portion of the regenerant solution of ethoxide may remain on the carbon and react with particular, or specific, functionalities of the carbon active sites, making it bond to the carbon, after exposure, and specifically within the mesopores. There is no evidence that the $NaOH/CH_3CH_2OH$ enlarged the pores or created any smaller pores as the values for the micropore surface area and pore volume were relatively unchanged. Nevertheless, any such changes are of minor concern since the micropores, which did not change, are the primary adsorption sites for micro-pollutants, such as pesticides, and organic contaminants on activated carbon (San Miguel et al., 2001). The results also suggested that any regenerant solution that remained on the carbon did not block the pathways for compounds to access the micropores.

There was a slight decrease in the concentration of carbonyl groups on the virgin carbon after exposure to the $NaOH/CH_3CH_2OH$ regenerant, compared to RO water, as shown in **Table 2**. In theory, the surface functional groups of the carbon, specifically the acidic sites, will be negatively charged or deprotonated by the presence of the alkaline regeneration solution (Boehm, 1994). The changes were observed to be not permanent because the transformation was reversible by re-adjusting the carbon pH to its initial pH during the conditioning step. An increase in the surface oxygen functional groups increases the polarity of the carbon, affecting the access of contaminants access to the basal plane of the carbon (Hutson et al., 2012).

The elemental composition percentages (**Table 2**) were in agreement with those reported in a previous study (Liu et al., 2008), although that study determined the entire oxygen content, including

the oxygen associated with carbon or as ash in the form of mineral oxides, by the difference of the carbon, nitrogen and hydrogen cumulative percentage. The elemental analysis showed that the chemical regeneration did not reduce the carbon content of regenerated carbon, which is consistent with the unchanging nature of the other properties described above, and confirmed again the advantages of chemical regeneration compared to thermal regeneration (San Miguel et al., 2002). The quantification of sodium through the acid digestion method showed an almost negligible amount of sodium was present in the carbon after regeneration by $NaOH/CH_3CH_2OH$. This indicated the absence of any significant residual concentration of regenerant solution in the carbon.

The almost negligible changes observed for the chemically regenerated carbon is particularly advantageous when compared to thermal regeneration, as the high temperatures and oxidizing conditions during the thermal regeneration process creates more macro-pores and decreases the yield of activated carbon (Guo and Du, 2012).

Table 2. Physical and chemical properties of carbon exposed to RO water and $NaOH/CH_3CH_2OH$ regenerant (n = 3, except for elemental composition where n = 1).

Properties	**Carbon + RO water**	**Carbon + $NaOH/CH_3CH_2OH$**
BET[a] surface area ($m^2\ g^{-1}$)	1222.6 ± 34.4	1149.0 ± 63.8
NLDFT[b] surface area ($m^2\ g^{-1}$)		
- Micropore surface area	837.7 ± 61.6	875.1 ± 15.9
- Mesopore surface area	47.5 ± 0.6	40.2 ± 3.1
- Macropore surface area	18.6 ± 0.3	16.7 ± 1.5
NLDFT pore volume ($cc\ g^{-1}$)		
- Micropore pore volume	0.32 ± 0.01	0.33 ± 0.01
- Mesopore pore volume	0.08 ± 0.00	0.10 ± 0.00
- Macropore pore volume	0.09 ± 0.00	0.09 ±0.01
Average pore diameter (nm)	0.48 ± 0.01	0.47 ± 0.01
Surface chemistry: oxygen-containing functional groups ($mmol\ g^{-1}$)		
- Phenols	0.12 ± 0.05	0.13 ± 0.03
- Lactonic	0.03 ± 0.02	0.03 ± 0.01
- Carboxylic	0.07 ± 0.03	0.06 ± 0.02
- Carbonyls	0.24 ± 0.03	0.22 ± 0.02
- Total acid	0.45 ± 0.02	0.44 ± 0.02
- Total basic	0.41 ± 0.03	0.42 ± 0.04
Elemental composition (%)		
- C	83.30	83.26
- H	0.63	0.78
- O[c]	1.18	1.35
- O[d]	14.15	13.81
- N	0.45	0.43
- S	1.42	1.68
- Na	0.01 ± 0.01	0.01 ± 0.01
- Al	0.03 ± 0.00	0.03 ± 0.00

Notes: [a]Brunauer–Emmett–Teller; [b]Non-Local Density Functional Theory; [c]Oxygen content that was associated with the carbon and measured using the unterzaucher method (Kirk and Wilkinson, 1970); [d]Oxygen content derived by the difference of other listed elements.

4. Conclusions

The performance of a novel $NaOH/CH_3CH_2OH$ regenerant for the chemical regeneration of exhausted granular activated carbon was investigated using rapid small-scale columns tests and two target pesticides, namely metaldehyde and isoproturon. The principal conclusions of the study are as follows:

- The $NaOH/CH_3CH_2OH$ solution was effective in regenerating the carbon exhausted by metaldehyde and isoproturon with a RE of 82% and 45%, respectively.
- The presence of non-desorbed pesticides on the carbon, remaining after the regeneration, decreased the performance of the carbon in the subsequent adsorption process.
- The results for metaldehyde as the target contaminant in dechlorinated tap water, showed that chemical regeneration (RE of ~52%) outperformed conventional thermal regeneration (RE of ~39%) after four equivalent regeneration cycles.
- Compared to virgin carbon, there were only slight changes in the thermodynamic parameters, including lower heat of adsorption values, in the adsorption of pesticides on the chemically regenerated carbon, which suggested that adsorption on the regenerated carbon involved weaker interactions.
- The results showed that the $NaOH/CH_3CH_2OH$ regenerant did not cause any significant changes in the physico-chemical properties of the carbon, within experimental error, indicating the benign nature of the regenerant.

Overall, the relatively high regeneration efficiency achieved by *in-situ* chemical regeneration, and the absence of any significant deleterious physical effects to the carbon, indicate the potential benefits of $NaOH/CH_3CH_2OH$ regeneration as an alternative to thermal regeneration. The findings of this study will be of interest to water utilities as they consider new methods of improving current GAC filter bed practice to manage the early breakthrough of weakly adsorbable contaminants, such as metaldehyde.

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