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Chemical regeneration of granular activated carbon: preliminary evaluation of alternative regenerant solutions†

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Granular activated carbon (GAC) is used in drinking water treatment plants worldwide to remove micro-pollutants such as pesticides. Early breakthrough of problematic micro-pollutants leads to frequent and costly thermal regeneration off-site. A potential alternative approach is to chemically regenerate GAC on-site (possibly *in situ*) with an appropriate solution capable of desorbing organic contaminants, having a range of physico-chemical properties. In this study, four types of regenerant solution were evaluated in batch tests for their ability to desorb five target contaminants. The solutions were: high purity water, sodium hydroxide, ethanol, and a mixture of sodium hydroxide and ethanol. The contaminants included: phenol and nitrobenzene, as representative aromatic compounds; clopyralid and metaldehyde, as poorly-adsorbed pesticides; and isoproturon, a well-adsorbed pesticide. Among the properties of the contaminants, their hydrophobicity and aqueous solubility had the most significant influence on the desorption efficiency. NaOH/CH₃CH₂OH was found to be more effective than individual solutions in desorbing the target contaminants, indicating an ability to desorb both hydrophobic and hydrophilic compounds. The NaOH/CH₃CH₂OH regenerant solution yielded desorption efficiencies in the range of approximately 40–90%, with the efficiency dependent on the contaminant. A thermodynamic study provided valuable fundamental information regarding the adsorption and desorption mechanisms, and the existence of two binding sites involving a weak physisorption and a stronger chemisorption-like interaction between the contaminants and the GAC.

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Water impact

The chemical regeneration of granular activated carbon (GAC) beds has been studied as a more cost-effective and flexible alternative to thermal regeneration. Chemical regeneration, using a novel regenerant solution, offers a low-energy and resource efficient process for the removal of poorly adsorbed organic micro-pollutants (*e.g.* pesticides), and to enhance the reliability of GAC operations in drinking water treatment practice.

1. Introduction

Granular activated carbon (GAC) adsorption has found wide application as a treatment process for the removal of natural organic matter, pesticides, taste and odour in water over many years.¹ During operation, these contaminants are adsorbed within the pores of GAC, which gradually become saturated with time. At saturation, or earlier if the filtrate quality is unacceptable, the GAC operation can no longer continue, and regeneration is carried out; this is a more cost-

effective option to lengthen the carbon life rather than disposal and carbon replacement.²

The presence of problematic, weakly adsorbable pesticides, such as metaldehyde³ and clopyralid⁴ (in the U. K.), causes early GAC bed exhaustion for these compounds, requiring more frequent GAC regeneration. The most common regeneration technique practised is thermal regeneration.¹ This technique has a disadvantage that the spent GAC commonly needs to be transported off-site to a specialized facility to perform it. In addition, the more frequent regeneration increases operational costs due to high carbon usage and reduced carbon service. During thermal regeneration, usually 5–10% of the carbon is lost due to attrition and excessive burn-off,⁵ and the lost carbon must be made up with virgin carbon. For these reasons, several *in situ* or on-site regeneration studies have been reported in the last

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30 years, as alternatives to thermal regeneration. One of these alternatives is chemical regeneration, which is a technique that can be performed *in situ* by exposing the spent GAC to chemical solvents to remove the contaminants,^{6,7} where the efficiency of chemical regeneration depends on the solvent used and the contaminants adsorbed.

Prior research on chemical regeneration has been limited in extent, but has considered both organic and inorganic solutions. For the former, organic solutions with solubilizing power and a lower molecular weight than the adsorbed contaminants were found to be the most effective regenerant solutions.^{8–10} A number of studies^{7,9,11} showed that alcohols such as ethanol and methanol were able to desorb phenol to a high degree. It was found that methanol was advantageous as a regenerant solution for activated carbon loaded by phenol,¹² as it had a high regeneration efficiency, could be recovered and is easily rinsed by water. However, methanol carries health concerns, owing to the formation of formaldehyde if digested, which represents a major disadvantage to its application in drinking water treatment. As an alternative, ethanol had a similar performance to methanol as a regenerant^{7,13} and has much lower potential toxicity than methanol.

With regard to inorganic regenerants, several studies have considered acid and basic solutions to achieve a high regeneration efficiency for the carbon exhausted by aromatic compounds, such as aniline and benzoic acid. In these cases, the change of pH of the solution may affect the surface charge of the adsorbent, and chemical reactions between adsorbate contaminants and regenerant solutions may occur which later facilitate desorption.^{9,14} However, the changes to the GAC surface properties by the acid or base may affect the adsorption of the contaminant after the regeneration process, which may be beneficial or detrimental to contaminant removal. An advantage of using acid and/or basic solutions as a solvent is that these chemicals are commonly used in water treatment for pH correction or softening, and may only present minimum practical difficulties, including the possibility of changing or coating the materials used in the current tanks and pipe works. Among the various potential inorganic chemicals, sodium hydroxide was found to be a relatively effective regenerant solution.^{15,16}

The effect of water at high temperatures was previously reported to be efficient in regenerating carbon exhausted by PFOS¹⁷ and other aromatic compounds.⁹ The high regeneration efficiency was attributed to the effect of elevated temperature on the thermodynamic equilibrium during the adsorption process.¹⁸ Not only does an increased temperature enhance the desorption process, it also increases the solubility of organic compounds in water^{9,18} by increasing their molecular kinetic energy. High temperature also reduces solution viscosity and consequently increases the diffusion rate of an adsorbate through the porous structure of the carbon during the desorption process.¹⁹

Despite a significant number of studies previously concerning chemical regeneration, the most suitable

regenerant solutions for desorbing a wide range of aqueous contaminants have not been identified to-date. In particular, the occurrence of weakly adsorbable pesticides in raw waters presents different challenges in determining the most suitable solution for regeneration. The adsorption and desorption mechanisms for these pesticides with GAC also have not been investigated systematically. Some earlier studies^{9,14} have reported regeneration efficiencies but without mentioning the desorption ratio achieved during chemical regeneration. This makes it unclear whether a higher degree of regeneration efficiency achieved was because of the desorption of contaminants, or the result of changes in the GAC properties which increased the adsorbate uptake in the subsequent adsorption phase. In this paper, we summarize an extensive study of the adsorption and desorption behaviour of particular target contaminants, and their desorption performance using different regenerant solutions. Calorimetric analyses have been conducted to provide important information relating to the adsorption mechanisms of the target contaminants on GAC.

2. Materials and methods

2.1. Materials and reagents

Virgin Filtrasorb 400 (Chemviron Carbon) GAC, with a granular size of 12 × 40 mesh (0.42–1.68 mm), effective size of 0.55–0.7 mm and maximum uniformity coefficient of 1.9,²⁰ was used throughout the tests; Filtrasorb 400 is a commercial carbon that is widely used in drinking water treatment works in the UK. Prior to use, a conditioning step was conducted, as follows: the carbon was washed using laboratory-grade reverse osmosis (RO) water until its pH was stable, dried at 105 °C to constant weight, and stored in a desiccator.

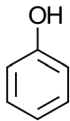
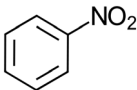
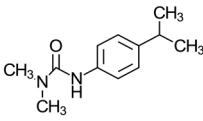
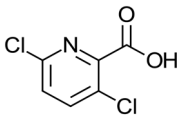
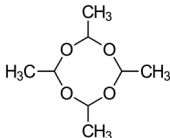
The target contaminants used in the tests were phenol (Fisher Scientific) and nitrobenzene (Honeywell) as representative aromatic compounds, and isoproturon (Sigma-Aldrich), clopyralid (Sigma-Aldrich) and metaldehyde (Acros Organics), which are pesticides that are commonly found in UK raw waters, where clopyralid and metaldehyde are often insufficiently removed by GAC (Table 1).

2.2. Target contaminant adsorption and desorption batch tests

The adsorption and desorption tests of the target contaminants were carried out in a batch system, as described in the following sections. Prior to the adsorption and desorption tests, the physico-chemical properties of the GAC used were investigated. The measurement of pH at the point of zero charge (pH_{pzc}) of the carbon followed the procedures conducted in previous study.²³ The surface area of carbon can be determined from nitrogen (N₂) adsorption-desorption isotherm data. The N₂ adsorption and desorption isotherms²⁴ were measured using an automatic Quantachrome Autosorb iQ3 instrument. A standardized Boehm titration was performed to identify the surface



Table 1 Physico-chemical properties of target contaminants^a

Properties	Phenol	Nitrobenzene	Isoproturon	Clopyralid	Metaldehyde
Chemical structure					
Molecular mass (g mol ⁻¹)	94.1	123.1	206.3	191.9	176.2
Solubility in water at 20 °C (g L ⁻¹)	80	1.90	0.07	7.85	0.22
Hydrophobicity (log <i>k_{ow}</i>)	1.46	1.85	2.50	1.06	0.12
Acid dissociation constant (p <i>K_a</i>)	9.99 (<i>T</i> = 25 °C)	3.98 (<i>T</i> = 0 °C)	NA	2.32 (<i>T</i> = 25 °C)	NA

^a Notes: values reported by PubChem²¹ and CRC Handbook of Chemistry and Physics.²² NA = not applicable.

functional groups of the carbon. The standardized procedures of the test followed those reported previously.^{25,26}

2.2.1. Adsorption studies: kinetics and isotherm. The adsorption kinetics of the different contaminants were conducted with a GAC mass of 1 g and a contaminant solution volume of 100 mL, which were agitated at 120 rpm, and samples were taken for analysis at designated contacting times. Single target contaminant adsorption and desorption kinetics were studied in order to determine the time required for the contaminants to reach equilibrium and the optimum desorption time, respectively. The initial concentrations were 2000, 400, 20, 20 and 20 mg L⁻¹ at pH 7.0 ± 0.1 for phenol, nitrobenzene, isoproturon, clopyralid and metaldehyde, respectively, representing their aqueous solubility. The adsorption study was conducted at room temperature (20 ± 1 °C). Adsorption kinetics were analysed using pseudo-first order, and pseudo-second order, kinetics models to describe the adsorption of the target contaminants. Numerous studies have been reported using these two types of kinetic models for the adsorption of pesticides on carbon.^{27–29}

The pseudo-first order kinetic model proposed by Lagergren³⁰ assumes that the rate of adsorption is proportional to the difference between the adsorbed quantity of the contaminant at equilibrium and the quantity adsorbed at a given time, as follows:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (1)$$

where *q* and *q_e* are the adsorption uptake (mg g⁻¹) at time *t* (min), and at equilibrium, respectively, and *k₁* is the pseudo-first order adsorption rate constant (min⁻¹). Integration of eqn (1), with the initial conditions of *t* = 0, and *q* = 0, gives the following explicit expression:

$$q = q_e(1 - e^{-k_1 t}) \quad (2)$$

The pseudo-second order kinetic model, as proposed by Ho and McKay,³¹ assumes that the rate of adsorption is proportional to the square of the difference between the adsorbed quantity of the contaminant at equilibrium and the quantity adsorbed at a given time, and the model is

expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (3)$$

where *k₂* is the pseudo-second order adsorption rate constant (g mg⁻¹ min⁻¹). Integration of eqn (3), with the initial conditions of *t* = 0, and *q* = 0, results in the following expression:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Adsorption isotherm tests were carried out based on a standard method.³² In summary, a varied amount of GAC F400 (0.01–1 g) and 100 mL of a target contaminant solution were transferred in to a borosilicate glass bottle and agitated on a platform shaker at 120 rpm for a predetermined time to reach equilibrium at room temperature (20 ± 1 °C). The solutions of target contaminant were prepared at initial concentrations of 2000, 400, 50, 100 and 100 mg L⁻¹ for phenol, nitrobenzene, isoproturon, clopyralid and metaldehyde at pH 7.0 ± 0.1, respectively. The pH of the solutions was adjusted using either 0.01 M NaOH or 0.01 M HCl prior to adsorption tests. The target contaminant concentrations in the solution before and after adsorption were determined using the analytical methods described in section 2.3. The contaminant uptake per unit mass of carbon, *q* (mg g⁻¹), was calculated by:

$$q = \frac{(C_0 - C)V}{m} \quad (5)$$

where *C₀* is the initial contaminant concentration in solution (mg L⁻¹), *C* is the contaminant concentration at equilibrium (mg L⁻¹), *V* is the volume of the target contaminant solution (l) and *m* is the mass of the carbon (g).

Both Langmuir and Freundlich isotherm models were fitted to the experimental data. These models are widely used to describe the adsorption equilibrium between an organic adsorbate and activated carbon.^{33,34} In the Langmuir isotherm model, the adsorbate is assumed to form a monolayer on the adsorbent surface.³⁵ The Langmuir model is expressed as:



$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (6)$$

where q_e is the adsorbate uptake at equilibrium (mg g^{-1}), q_m is the adsorbate uptake to completely form a monolayer on the adsorbent surface (mg g^{-1}), k_L is the Langmuir constant related to the affinity of the binding sites (L mg^{-1}) and C_e is the adsorbate concentration in the solution at equilibrium (mg L^{-1}). In contrast, the Freundlich isotherm model is an empirical relationship that represents a multilayer adsorption process on heterogeneous surfaces,³⁶ and is expressed as:

$$q_e = k_F C_e^{1/n} \quad (7)$$

where k_F is the Freundlich constant, related to the favourability of the adsorption process ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$) and n is a dimensionless constant related to the adsorption driving force or the surface heterogeneity.³⁷

2.2.2. Adsorption and desorption tests. Initially, contaminant adsorption was carried out at pH 7.0 + 0.1, by adding 1 g of GAC to 100 mL of a contaminant solution in a borosilicate glass bottle. The bottle was agitated using a platform shaker at 120 rpm for a predetermined time until the adsorption process reached equilibrium. Subsequently, the adsorbate solution was decanted and then filtered using a Whatman filter paper grade 1 (11 μm pore diameter) for phenol, nitrobenzene, isoproturon and clopyralid, and a nylon membrane syringe filter (Gilson Scientific Ltd, 0.2 μm pore diameter) for metaldehyde. The different method of filtration for metaldehyde to the other contaminants was because of the difference of analytical method used as described subsequently. The initial concentration of each target contaminant of phenol, nitrobenzene, isoproturon, clopyralid and metaldehyde was 2000, 400, 20, 20 and 20 mg L^{-1} , respectively; these initial concentrations were based on the aqueous solubility of the target contaminants and to enable their accurate determination in samples following adsorption and desorption.

Upon completion of the adsorption tests, 100 mL of a selected regenerant solution was added to the bottle, which contained the exhausted GAC, and agitated for a predetermined time to enable desorption. The solution was then decanted and filtered, and the pH adjusted to lie in the range of 6–8 using 0.1 M NaOH or 0.1 M H_3PO_4 , prior to the detection and quantification of the desorbed contaminant. The desorption tests were conducted using four regenerant solutions, namely, RO water at three different temperatures of 20, 50 and 80 $^\circ\text{C}$, sodium hydroxide (NaOH), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and a mixture of sodium hydroxide and ethanol ($\text{NaOH}/\text{CH}_3\text{CH}_2\text{OH}$).

The efficiency of the chemical regeneration can be quantified based on the ability of a regenerant solution to recover the adsorbed contaminant, and calculated as desorption efficiency (DE), as follows:

$$\text{DE}(\%) = \frac{q_{\text{des}}}{q_{\text{ads}}} \times 100\% \quad (8)$$

where DE is the ratio of the amount of contaminant desorbed per gram of carbon during the regeneration process (q_{des}) to the initial carbon adsorption capacity of the target contaminant (q_{ads}).

2.3. Detection and quantification of target contaminants

The concentrations of phenol, nitrobenzene, isoproturon and clopyralid were determined by UV-visible spectrophotometry (Shimadzu UV-2401PC UV-vis spectrophotometer), and metaldehyde concentrations were determined by ultra-high performance/pressure liquid chromatography (UHPLC) with quadruple-time of flight (Q-TOF) spectrometry (Waters Synapt G2-Si high definition mass spectrometry) using electrospray ionization (ESI) technique. The optimal detection wavelengths used for phenol, nitrobenzene, isoproturon and clopyralid analysis were 269, 268, 240 and 280 nm, respectively.

Metaldehyde was detected and quantified in the ESI positive mode. An Acquity UPLC BEH C18 column (2.1 \times 100 mm, 1.7 μm particle size, Waters Ltd) was used and maintained at 40 $^\circ\text{C}$ for the analysis. The mobile phases used were A: LC-MS grade water and 0.1% of formic acid (VWR) and B: LC-MS grade acetonitrile (Honeywell). The gradient program was: 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 min isocratic of 30% B (v/v). Total analysis time was 10 min, the flow rate 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 cartridge (Waters Sep-Pak C18, 55–105 μm particle size) prior to injection. The instrument was set to detect metaldehyde ions of 199 m/z in MS/MS mode with a retention time of 2.45 min.

2.4. Investigation of reaction products during chemical regeneration

Possible reaction products arising from the regenerant solution and target contaminants were investigated by mass spectrometry, where identification was based on the structural information obtained from fragmentation and parent compound data.³⁸ A direct analysis using an atmospheric pressure solid analysis probe (ASAP) technique using Q-TOF spectrometry (Waters Synapt G2-Si high definition mass spectrometry) was carried out for a rapid identification of products from phenol, nitrobenzene, isoproturon and clopyralid, while the ESI technique was applied for metaldehyde, as metaldehyde is easily degraded at the high temperature required to perform ASAP technique.

The mass spectrometry parameter settings were as follows: the source and desolvation temperature were set at 120 and 150 $^\circ\text{C}$, respectively; the desolvation and cone gas flows were 400 and 30 L h^{-1} , respectively; the corona current was set at 5 μA , and the sampling cone voltage to 35 V. The instrument was operated in positive mode. Prior to identification, the



capillary glass sample holder was rinsed using LC-MS grade methanol (VWR), and baked at 400 °C for 3 min.

2.5. Heat of adsorption using a calorimetric titration method

Calorimetric tests were carried out using a VP isothermal titration calorimeter (ITC) from Microcal, Inc. The heat exchange between the carbon and target contaminant was measured at 298.15 K (25 °C) to determine the thermodynamic parameters during the adsorption process. The ITC has been used widely to investigate interactions between molecules as it has the ability to accurately measure the Gibbs energy, enthalpy and entropy associated with the interactions.^{39,40} The target contaminants investigated were phenol, isoproturon and metaldehyde, as described subsequently.

A well-dispersed suspension of F400 carbon in water (immersed for >24 h) at a concentration of 2 g L⁻¹, and target contaminant solutions at a concentration of 0.25 mM, were thoroughly degassed for 5 min prior to each test to remove air bubbles from the samples. The suspension was placed in the reaction cell with a volume of 1.4 mL and a target contaminant was loaded into the 300 µL injection syringe. The titration was carried out with 1 injection of 4 µL, followed by 24 injections of 10 µL aliquots, at 180–300 s intervals between two injections, with a stirring speed of 300 rpm. The test procedure followed that used in previous studies of metal ions and methylene blue adsorption on carbon materials.^{41–43}

The ITC data were automatically analysed using the Microcal Origin 7.0 software. All the data were blank corrected for the heat of dilution of target contaminant and water, and the heat of carbon and water interactions. The thermodynamic parameters, such as K_a (binding constant) and $\Delta_{\text{ads}}H$ (enthalpy or heat of adsorption) were predicted as adjustable parameters in the fitting procedure of the Origin 7.0 software. Data were fitted using a non-linear least-squares (Levenberg–Marquardt) algorithm. The adsorption $\Delta_{\text{ads}}G$ (Gibbs free energy) and $\Delta_{\text{ads}}S$ (entropy) were calculated using the following thermodynamic relationship, where T is the temperature of the measurement (K).

$$\Delta_{\text{ads}}G = -RT \ln K_a = \Delta_{\text{ads}}H - T\Delta_{\text{ads}}S \quad (9)$$

3. Results and discussion

The physico-chemical properties of the GAC F400 used throughout the tests are summarized in Table 2.

3.1. Adsorption kinetics of target contaminants

The results showed that the adsorption of the contaminants reached equilibrium after approximately 24 h (1440 min), except for metaldehyde, which required at least 48 h (2880 min). As can be seen in Fig. 1, the initial adsorption of all compounds was rapid, and for phenol, nitrobenzene and

Table 2 Physico-chemical properties of GAC F400 used throughout the tests (variations represent the standard deviation of triplicate measurements)

Properties	Value
pH _{pzc}	8.2
Brunauer–Emmett–Teller (BET) surface area (m ² g ⁻¹)	1222.6 ± 34.4
Average pore width (nm)	0.48 ± 0.01
Surface chemistry: oxygen-containing functional groups (mmol g ⁻¹)	
Phenol	0.119 ± 0.051
Lactonic	0.028 ± 0.023
Carboxylic	0.065 ± 0.027
Carbonyl	0.237 ± 0.028
Total acid	0.449 ± 0.018
Total basic	0.412 ± 0.029

isoproturon, the adsorption occurred mostly in the first 60 min, owing to the strong affinity between the GAC and these contaminants. In all cases, the results were well described by a pseudo-second order kinetic model ($R^2 = 0.99–1.00$), in comparison to a pseudo-first order model (Table 3 and Fig. 1), and indicated that the adsorption rate was related to the compound hydrophobicity and solubility. Thus, for isoproturon, clopyralid and metaldehyde, at the same initial concentration of 20 mg L⁻¹, the calculated adsorption rate (k_2) and adsorption capacity (q_e) decreased in the order of isoproturon > clopyralid > metaldehyde, which corresponded directly to their decreasing hydrophobicity as indicated by their octanol–water partition coefficient ($\log k_{ow}$) (Table 1). A similar relationship between $\log k_{ow}$ and organic contaminant adsorption by carbon was also reported previously,³⁶ and the low adsorption capacity of metaldehyde by activated carbon also reported in a number of previous studies.^{28,44,45}

3.2. Adsorption isotherms of target contaminants

The adsorption equilibrium results for the target contaminants are shown in Fig. 2, and the corresponding model parameters are summarized in Table 4. Comparison with the experimental data indicated that the Langmuir model described the adsorption of the contaminants more closely, based on the correlation coefficient (R^2) values. From the Langmuir model, a GAC monolayer uptake capacity of the target contaminants was derived, and the results indicated that the nitrobenzene and isoproturon had a higher q_m value than phenol, clopyralid and metaldehyde. In the Freundlich model, the constant, k_F , explains the favourability of the adsorption process of contaminants. As shown in Table 4, the k_F values of the target contaminants show a similar trend to the q_m values of the Langmuir model. The greater uptake of nitrobenzene and isoproturon by the carbon is attributed to their relatively greater hydrophobic nature, as indicated by their higher octanol–water partition coefficients ($\log k_{ow}$), compared to the other contaminants.

The q_m value of 192 mg g⁻¹ for phenol was similar to that reported previously.⁴⁶ Nitrobenzene was found to have the



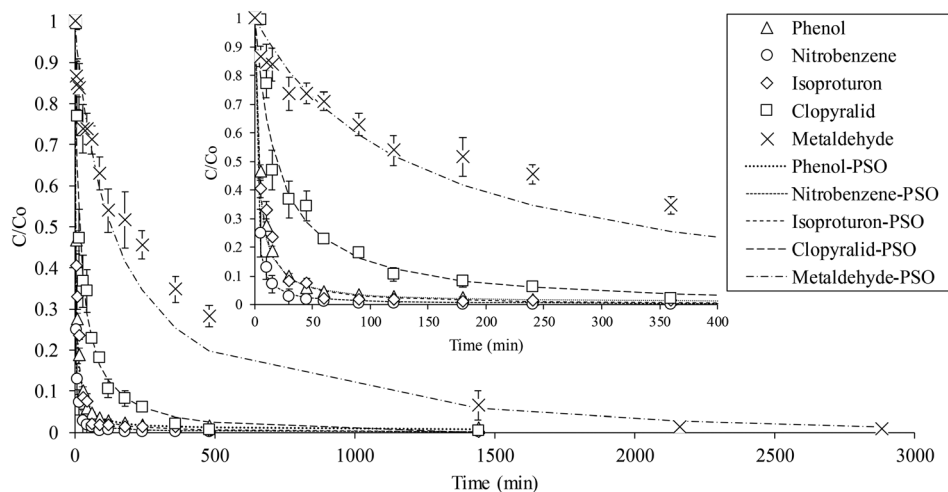


Fig. 1 Adsorption kinetics of target contaminants using F400 shown with theoretical values obtained by kinetic analysis using pseudo-second order (PSO) model (inset figure highlights initial period 0–400 min; error bars represent one standard deviation for duplicate measurements).

Table 3 Parameters obtained from fitting experimental data to the pseudo-first (PFO) and pseudo-second (PSO) kinetic models (20 ± 1 °C)

Target contaminant	C_0 (mg L ⁻¹)	Pseudo-first order (PFO)			Pseudo-second order (PSO)		
		q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
Phenol	2000	3.3	0.010	0.71	101.0	0.003	1.00
Nitrobenzene	400	1.8	0.016	0.68	40.2	0.022	1.00
Isoproturon	20	0.6	0.011	0.71	2.2	0.147	1.00
Clopyralid	20	1.2	0.012	0.96	2.2	0.026	0.99
Metaldehyde	20	1.2	0.002	0.98	2.1	0.003	0.99

highest q_m value (435 mg g⁻¹) of all the target contaminants, most likely because of the combination of a high log k_{ow} , low aqueous solubility and low molecular weight; the q_m was slightly lower to that reported previously.⁴⁷ For isoproturon, q_m was 250 mg g⁻¹, which was slightly lower than the value reported in an earlier study⁴⁸ where the adsorption test was conducted at 30 °C. The adsorption performance of clopyralid has received little attention previously in scientific terms; however, like metaldehyde, a significant number of water quality compliance failures have been reported in the UK for clopyralid,⁴ which indicates a relatively low adsorption by activated carbon. In agreement with this, the GAC uptake of clopyralid in this study was relatively low ($q_m = 143$ mg g⁻¹), and similar to the value of q_e of ~150 mg g⁻¹ (for $C_e = 50$ mg L⁻¹) reported in a recent study.⁴⁹ Lastly, for metaldehyde, the q_m value of 137 mg g⁻¹ found in this study was lower than the value of 320 mg g⁻¹ reported by Salvestrini *et al.*,⁵⁰ but greater than the values of 71 mg g⁻¹ and 28.3 mg g⁻¹ reported by Tao and Fletcher²⁸ and Li *et al.*,⁴⁵ respectively. These differences may be explained by differences in the properties of the GAC used in the studies, such as the carbon pore size distribution, particle size and surface chemistry. Busquets *et al.*⁴⁴ previously reported that there was no correlation between the carbon surface area and metaldehyde adsorption, which suggested that the adsorption was governed by more complex effects than simply physisorption. However, isotherm data on their own

are not sufficient to elucidate the adsorption mechanisms, and need to be complemented by additional tests, such as desorption and thermodynamics;³⁷ these were carried out in this study and the results are summarized in subsequent sections of this paper.

3.3. Desorption of single contaminants

The five target contaminants and four alternative regenerant solutions were used to investigate the performance of chemical regeneration, and the influence of pH, compound solubility and interactions between the contaminant, regenerant and activated carbon during the regeneration process. The maximum desorption efficiency (DE) using each regenerant solution was achieved within 120 min; details of the desorption kinetics are given in Fig. S1–S3, in ESI.†

3.3.1. Regeneration by RO water and the effect of temperature. The DE in water depends strongly on the aqueous contaminant solubility and phenol was found to have the highest DE at all the water temperatures studied (20, 50 and 80 °C) (Table 5) compared to the other contaminants, as it has the highest aqueous solubility (Table 1). A previous study⁵¹ suggested that physisorption is the main adsorption mechanism of phenol onto activated carbon. However, the low DE of phenol at 20 °C indicated that even though phenol is moderately soluble in water^{12,52}



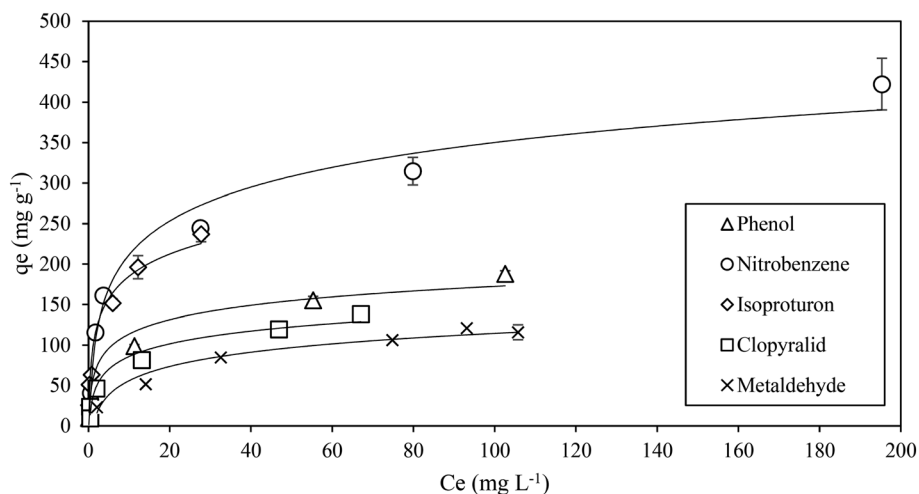


Fig. 2 Comparison of experimental adsorption isotherm data among the target contaminants (error bars represent one standard deviation for duplicate measurements).

Table 4 Parameters obtained from fitting experimental data to the Langmuir and Freundlich isotherm models (20 ± 1 °C)

Target contaminant	Langmuir isotherm			Freundlich isotherm		
	q_m (mg g ⁻¹)	k_L (L mg ⁻¹)	R^2	k_F (mg g ⁻¹ (L mg ⁻¹) ^{1/n})	n	R^2
Phenol	192.3	0.16	0.99	33.5	2.49	0.94
Nitrobenzene	434.8	0.08	0.98	74.2	2.87	0.89
Isoproturon	250.0	0.51	0.99	69.5	2.50	0.97
Clopyralid	142.9	0.18	0.99	24.7	2.32	0.89
Metaldehyde	136.9	0.01	0.99	17.2	2.35	0.99

at room temperature, it was not able to achieve a high degree of desorption.

The low desorption efficiency by water of nitrobenzene and isoproturon was attributed to their limited water solubility and relatively high $\log k_{ow}$. Clopyralid and metaldehyde, which were only weakly adsorbed by carbon, also had a low desorption efficiency, suggesting that the potential energy of adsorption was strong enough to prevent desorption. Although Tao and Fletcher²⁸ reported a modest amount (26%) of metaldehyde leaching from an exhausted GAC column during a water washing process, no significant leaching was observed in this study. A low desorption (<9%) of metaldehyde using water at room temperature in a batch system was also reported by Li *et al.*⁵³ A plausible explanation is that the tests in this study were conducted in a batch system where pore blockage may affect the desorption efficiency.⁵⁴

Previously, it has been reported that boiling water performed effectively in desorbing phenol from exhausted carbon,¹⁹ as the high temperature increases phenol diffusivity in water. Similarly, in this study the results showed an increasing desorption efficiency for phenol with increasing water temperature, but this was still modest (<24%) even at 80 °C (Table 5). For metaldehyde, the desorption efficiency was less than 6% at 80 °C and little mineralization was observed, suggesting that high water temperature did not have a significant impact on the

desorption or degradation of adsorbed metaldehyde. A recent study by Rolph *et al.*⁵⁵ reported that metaldehyde degraded in water at temperatures >60 °C and the DEs yielded in this study suggested that metaldehyde was more stable when adsorbed to the carbon and not degraded at high temperature (80 °C). The low DE of the other target contaminants, nitrobenzene, isoproturon and clopyralid, in water at 80 °C (Table 5) demonstrated that these contaminants were strongly adsorbed to the carbon, which suggested that their solubility in water greatly affected the DE values.

Overall, the results indicated that water was unable to achieve sufficient desorption of the target contaminants from exhausted carbon, and may only be effective for desorbing highly water-soluble contaminants.

3.3.2. Sodium hydroxide (NaOH). The desorption results for different concentrations of sodium hydroxide (NaOH) are summarized in Table 6. For phenol, it was evident that irrespective of the NaOH concentration the high pH of these solutions (>13.0) produced a similar DE of approximately 50% (42.5–54.5%). Phenol reacts with NaOH to produce a soluble phenolate salt^{9,14,56} which is readily removed during the desorption process; this is also facilitated by the electrostatic repulsion between the negatively charged carbon surface and phenolate anion. It was noted that the phenol desorption efficiency appeared to increase slightly with NaOH concentration, between 0.1 and 1 M, but decreased at 2 M



Table 5 Desorption efficiencies for RO water at different water temperatures ($n = 2$)

Temperature (°C)	DE (%) for the carbon exhausted with target compound				
	Phenol	Nitrobenzene	Isoproturon	Clopyralid	Metaldehyde
20	3.3–3.9	0.1 ^a	1.3–2.2	2.5–2.6	2.3–3.1
50	18.2–18.6	0.2 ^a	0.9–1.4	2.8–3.1	2.4–2.5
80	21.1–23.6	0.4 ^a	5.1–5.4	14.0–14.3	4.7–5.9

^a The DE values for duplicate measurements have a standard deviation less than 0.01%.

Table 6 Desorption efficiencies for sodium hydroxide at 20 ± 1 °C ($n = 2$)

Concentration (M)	DE (%) for the carbon exhausted with target compound				
	Phenol	Nitrobenzene	Isoproturon	Clopyralid	Metaldehyde
0.1	46.8–48.6	0.1–0.2	4.2–4.2	3.2–3.6	4.2–4.8
0.5	47.4–51.7	0.1–0.2	2.6–4.0	3.1–3.9	3.0–3.4
1	50.7–54.5	0.2 ^a	3.2–5.3	4.2–4.3	3.2–6.7
2	42.5–49.1	0.3 ^a	4.1–5.3	4.8–5.3	2.9–4.8

^a The DE values for duplicate measurements have a standard deviation less than 0.01%.

NaOH. Martin and Ng⁹ suggested that this can be attributed to OH⁻ adsorption onto the carbon which may hinder the desorption process. Another plausible explanation is that higher NaOH concentrations may reduce the solubility of the target contaminants by a ‘salting out’ effect.⁵⁷

For nitrobenzene, isoproturon, clopyralid and metaldehyde, the DE of the NaOH solutions was no greater than water at room temperature. Nitrobenzene is known to have a strong affinity for activated carbon (Fig. 2) and predominantly in its neutral form in the pH range of 2–14; an almost negligible DE of nitrobenzene with NaOH was also reported in a previous study.⁵⁸ Isoproturon showed a similar affinity for activated carbon as nitrobenzene, and does not dissociate in water at any pH; increasing the NaOH concentration did not enhance the desorption of either nitrobenzene or isoproturon to any significant extent.

Clopyralid exists almost entirely in a dissociated, anionic form in neutral and high pH solutions and therefore a substantial desorption of clopyralid in high pH solution was anticipated, owing to electrostatic repulsion between the dissociated compound and the negatively charged carbon surface. However, desorption was found to be poor suggesting the importance of other factors. Nevertheless, the effect of charge interactions was indicated by the small

increasing in DE with increasing NaOH concentration (Table 6).

The very low desorption efficiency for metaldehyde using NaOH was most likely because of the limited solubility of the compound in the regenerant solution.

3.3.3. Ethanol (CH₃CH₂OH). The results using ethanol (Table 7) showed that the target contaminants with a relatively high hydrophobicity ($\log k_{ow} > 1.4$), namely, phenol, nitrobenzene and isoproturon, had a high DE, compared to clopyralid and metaldehyde, which had lower hydrophobicity ($\log k_{ow} < 1.4$) and a DE less than 15%. In addition to hydrophobicity, it was speculated that the DE using ethanol was related to the solubility of the target contaminant in ethanol. However, even though the solubility of clopyralid and metaldehyde in ethanol was greater than in water, this did not result in a significant DE, indicating that the two contaminants preferred to remain adsorbed on the activated carbon rather than solvate in ethanol.

As expected, the DE values for the compounds decreased with the concentration of ethanol in water (Table 7). As ethanol is highly soluble in water, the presence of water adversely affected the ability of ethanol to desorb the target contaminants⁹ as the water molecules will form a hydration shell around ethanol, making it too large to enter the carbon pores.

Table 7 Desorption efficiencies for ethanol at 20 ± 1 °C ($n = 2$)

Concentration (% v/v)	DE (%) for the carbon exhausted with target compound				
	Phenol	Nitrobenzene	Isoproturon	Clopyralid	Metaldehyde
99	62.1–62.6	43.6–44.6	67.9 ^a	8.8–11.1	9.5–14.6
80	58.9–60.1	35.0–37.1	39.0–39.4	3.7–3.8	6.8–9.9

^a The DE values for duplicate measurements have a standard deviation less than 0.01%.



Table 8 Desorption efficiencies by a mixture of sodium hydroxide and ethanol at 20 ± 1 °C ($n = 2$)

Concentration (M of NaOH and % v/v of CH ₃ CH ₂ OH)	DE (%) for the carbon exhausted with target compound				
	Phenol	Nitrobenzene	Isoproturon	Clopyralid	Metaldehyde
0.1 in 99	84.0–88.2	35.4–46.8	44.6–45.0	75.9–79.4	50.0–53.4
0.1 in 80	82.1–89.0	34.3–35.5	35.2 ^a	73.8–77.1	60.0–68.6
0.5 in 80	78.6–82.8	31.4–32.1	37.6–37.7	80.5–83.0	77.6–82.4

^a The DE values for duplicate measurements have a standard deviation less than 0.01%.

3.3.4. A mixture of sodium hydroxide and ethanol (NaOH/CH₃CH₂OH). In a previous study, a mixture of sodium hydroxide and methanol showed a capability for regenerating carbon exhausted by phenol, aniline, benzoic acid and nitrobenzene, and it was postulated that changes in the surface properties of the carbon were responsible for the desorption of the contaminants.¹⁴ As mentioned previously, the potential use of methanol in practice is not feasible owing to toxicity concerns. In this study, three different mixtures of NaOH/CH₃CH₂OH were considered and the results are shown in Table 8. In general, it can be seen that all mixtures achieved substantial degrees of desorption for all the contaminants, and particularly for the hydrophilic compounds where the DE values were much greater than those for NaOH or ethanol individually (Tables 6 and 7, respectively).

When NaOH is dissolved in ethanol, both hydroxide and ethoxide ions are present in solution.⁵⁹ Ethoxide has been shown to be able to neutralize acidic functional groups on carbon surfaces using the Boehm titration method, which is employed widely to identify the surface chemistry of any carbon materials.^{60,61} As the adsorption of organic contaminants on GAC can be through interactions with the surface functional groups, the presence of ethoxide may disturb these interactions and facilitate contaminant desorption. As shown previously, hydroxide alone also has an ability to interact with the surface functional groups on the carbon,⁶² but ethoxide is a stronger base and more aggressive than hydroxide as atoms in the alkane chain donate electron density to oxygen, allowing ethoxide to be more polarizable. The aggressive nature of ethoxide thus resulted in the greater DE of clopyralid and metaldehyde observed with NaOH/CH₃CH₂OH compared to only NaOH. Additionally, the use of ethanol as a co-solvent is more advantageous as the contaminants are more soluble in ethanol than in water. It is well known that organic contaminants adsorb through different mechanisms on the carbon, such as through donor acceptor complex interactions,^{63,64} where carbonyl groups on the surface act as an electron donor and the contaminant as an electron acceptor. Ethoxide, which has a high nucleophilic property, is strong enough to neutralise the carbonyl groups on the carbon surface through hemiacetal reactions^{65,66} and thereby promote the desorption of the adsorbed contaminants.

The results for the NaOH/CH₃CH₂OH combination are very promising in terms of chemical desorption of adsorbed contaminants and recovery of surface sites for subsequent adsorption, thereby increasing the duration of the GAC bed life prior to full thermal regeneration or carbon disposal.

3.4. Fate of the contaminants

A possible reaction between the NaOH/CH₃CH₂OH mixture and adsorbed contaminants was investigated using mass spectrometry to further clarify the desorption mechanisms involved. It was found that only phenol transformed upon exposure to a mixture of NaOH/CH₃CH₂OH (results are given in Table S1, in ESI†). In this case phenolate ion was formed as phenol has a pK_a value of 9.99 as shown in Table 1, supporting the previous notion that phenol desorbed from the carbon surface because of the formation of a water-soluble phenolate ion. The absence of any detectable transformation or chemical reaction for the other target contaminants suggested that the desorption of these contaminants was affected by their solubility in the mixture, and/or a reduced affinity for the carbon surface as a result of changes to the properties of the carbon caused by the mixture. A similar finding was observed with aromatic contaminants, such as nitrobenzene, which is strongly adsorbed to the carbon, but where its desorption was driven by the decrease of carbon affinity.¹⁴

3.5. Heat of adsorption

In order to provide more information regarding the mechanisms of adsorption and desorption of the contaminants, a calorimetric study was conducted involving three of the contaminants: phenol to represent general organic compounds, isoproturon to represent hydrophobic compounds and metaldehyde to represent hydrophilic compounds. The results of the tests are summarized in Fig. 3 and Table 9, which show that the adsorption of the target contaminants occurs at two types of binding sites (denoted as 1 and 2) on the carbon and these binding sites might be identical or dependent. In all cases it was found that the magnitude of the respective binding constants was $K_{a2} > K_{a1}$, which meant that the binding to the first site energetically favoured the subsequent binding to the other site.⁶⁷

For the first site (site 1), which is a relatively weak binding site ($\Delta_{\text{ads}}G = -22.1$ kJ mol⁻¹ for phenol, -14.9 kJ mol⁻¹ for



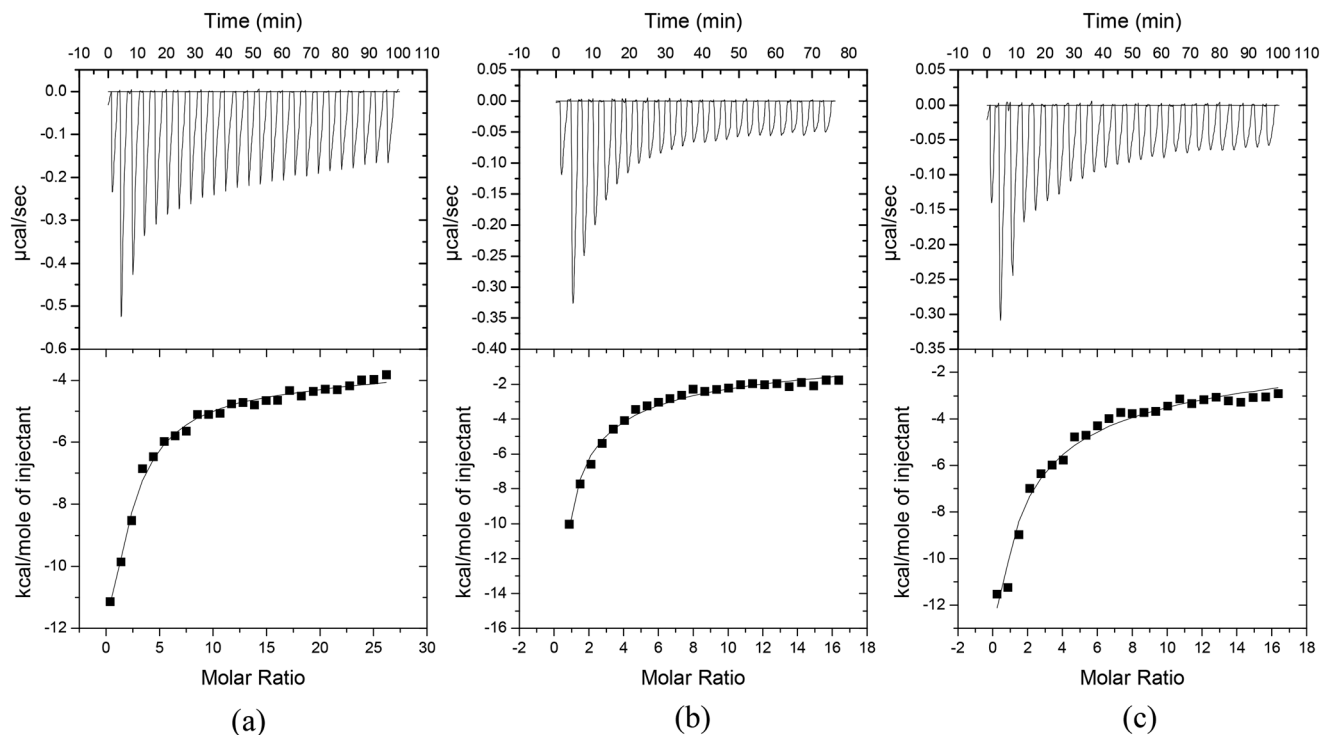


Fig. 3 Real-time thermograms (top) and binding isotherms after blank subtraction (bottom) for the titration of (a) phenol, (b) isoproturon and (c) metaldehyde against activated carbon F400.

Table 9 Thermodynamic parameters (see eqn (2)) of contaminant adsorption on F400 at 298.15 K (variations represent the standard deviation for duplicate measurements)

Target contaminant	Site	K_a (M^{-1})	$\Delta_{ads}G$ ($kJ\ mol^{-1}$)	$\Delta_{ads}H$ ($kJ\ mol^{-1}$)	$T\Delta_{ads}S$ ($kJ\ mol^{-1}$)
Phenol	(1)	$(7.5 \pm 0.9) \times 10^3$	-22.1 ± 0.3	-53.2 ± 0.4	-31.3 ± 0.7
	(2)	$(8.0 \pm 0.7) \times 10^5$	-33.7 ± 0.2	36.9 ± 1.8	70.7 ± 1.6
Isoproturon	(1)	$(4.4 \pm 0.2) \times 10^2$	-14.9 ± 0.4	-123.2 ± 7.9	-108.3 ± 7.6
	(2)	$(5.9 \pm 0.2) \times 10^5$	-32.7 ± 0.2	146.2 ± 14.5	171.4 ± 3.6
Metaldehyde	(1)	$(2.0 \pm 0.8) \times 10^2$	-13.1 ± 0.1	-186.7 ± 1.9	-173.5 ± 2.1
	(2)	$(4.3 \pm 0.5) \times 10^5$	-32.2 ± 0.3	179.2 ± 7.2	211.3 ± 6.9

isoproturon and $-13.1\ kJ\ mol^{-1}$ for metaldehyde), the values of all of the thermodynamic parameters were negative, indicating that the adsorption at this site is spontaneous and thermodynamically favourable. This site may 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 *via* the water molecules with the hydrophilic carbon surface.⁶⁰ The adsorption at this site is where the carbon surface is covered with a monolayer of the contaminant molecules. A higher negative value of phenol adsorption ($\Delta_{ads}G$) reflects a more energetically favourable adsorption compared to isoproturon and metaldehyde,⁶⁸ which is possibly because the smaller molecular size of phenol enables it to penetrate to, and adsorb in, deeper pores of the carbon. Isoproturon has a higher negative value of $\Delta_{ads}G$ than metaldehyde which may reflect its greater hydrophobicity, and thus the adsorption of isoproturon at

site 1 was more thermodynamically favourable compared to metaldehyde. Phenol had the highest desorption efficiency using water at 80 °C compared to the other contaminants as it is the most water-soluble, and this suggested that physisorption is an important adsorption mechanism of phenol but not a dominant mechanism for isoproturon and metaldehyde adsorption. The negative value of the entropy ($T\Delta_{ads}S$) of the system describes the transfer of the contaminant from the solution bulk phase to the solid-liquid interface, which decreases the entropy of the system and the degree of freedom of the contaminant.⁶⁹

The second site (site 2) is a stronger binding site than site 1 ($\Delta_{ads}G = -33.7\ kJ\ mol^{-1}$ for phenol, $-32.7\ kJ\ mol^{-1}$ for isoproturon and $-32.2\ kJ\ mol^{-1}$ for metaldehyde). 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 value of the $T\Delta_{ads}S$ suggested that the contaminant molecules on the



carbon surface adsorbed in a multilayer arrangement. This arrangement commonly involves a weaker strength of intermolecular force, such as van der Waals, dispersion and electrostatic interactions,⁶⁰ thus the molecules that are furthest from the carbon surface or that have lower adsorption potential energy become less stable and may desorb, becoming less arranged. The formation of multilayers is expected before the contaminants fill the higher energy adsorption sites (high $\Delta_{\text{ads}}H$ or low $-\Delta_{\text{ads}}H$).⁷⁰ Taking into account that the $\Delta_{\text{ads}}H$ values of isoproturon and metaldehyde exceeded 100 kJ mol^{-1} , and the process was endothermic at this site, the adsorption mechanisms of isoproturon and metaldehyde most likely involved chemisorption-like interactions. Bansal and Goyal⁶⁰ reported that the heat of chemisorption is usually in the range of $40\text{--}400 \text{ kJ mol}^{-1}$ and Tong *et al.*⁷¹ suggested that a strong H-bond between carbon and a micropollutant could occur with an enthalpy value of $\sim 100 \text{ kJ mol}^{-1}$. As previously reported,^{63,64} organic contaminants are able to form strong donor-acceptor complexes with oxygen functional groups on the carbon surface, such as carbonyl groups, which has a large dipole moment compared to the carboxylic groups. This kind of interaction requires activation energy and the extent of the adsorption depends upon the temperature of adsorption. Furthermore, Ferro-García *et al.*⁷² suggested that surface carbonyl groups play an important role for chemisorbed organic contaminants. In the evaluation of the desorbability of target contaminants in this study, a higher degree of desorption was achieved using the mixed NaOH/ $\text{CH}_3\text{CH}_2\text{OH}$ solution, which was attributed to its ability to interact with, and weaken, the carbonyl functional group on the carbon.

A study conducted by Busquets *et al.*⁴⁴ showed that metaldehyde adsorption onto activated carbon was independent of the carbon's specific surface area, which indicated that the adsorption mechanism was more complex than just physisorption. The results from this study also support those reported previously, including both a theoretical study⁷³ and a laboratory investigation²⁸ which indicated that metaldehyde adsorption involves hydrogen bonding with carbon surface functional groups, with or without mediation by water molecules. Other phenomena such as van der Waals interactions and the thermodynamic gradients may also be contributory mechanisms for metaldehyde adsorption. The heat-consuming processes during the contaminant adsorption can also be attributed to the energy required to break hydrogen bonds between the contaminant and water in the bulk phase, and between the surface functional groups of the carbon and water. To interact with these functional groups, the contaminants have to displace possibly more than one water molecule from their adsorption site, resulting in the endothermic nature of the process. The endothermic nature of the adsorption process was also reported for phenol and metaldehyde^{28,74} whereby the contaminant uptake increased with the solution temperature.

Additionally, the large and positive value of $\Delta_{\text{ads}}H$ is most likely due to the release of water molecules from the displacement of the contaminants at the adsorption sites.^{43,69} The high entropy of isoproturon adsorption onto carbon also might be due to the hydrophobic interaction involved.³⁹ The unfavourable nature of positive $\Delta_{\text{ads}}H$ value for the second site, which would make a reaction non-spontaneous, is counteracted by the positive $\Delta_{\text{ads}}S$ values and negative value of $\Delta_{\text{ads}}G$, indicating that the contaminant adsorption process is spontaneous.⁷⁵

In summary, the calorimetric investigation suggested that isoproturon and metaldehyde were more strongly bonded compared to phenol. This is consistent with the results of the desorption tests using different types of regenerant solution, which showed it was more difficult to desorb isoproturon and metaldehyde from GAC, compared to phenol.

4. Conclusions

To evaluate the feasibility of a novel on-site chemical regeneration of GAC, an adsorption and desorption study has been conducted using five organic compounds (known contaminants) of different physico-chemical properties (phenol, nitrobenzene, isoproturon, clopyralid and metaldehyde) and four regenerant solutions (laboratory grade RO water at 20, 50 and 80 °C, NaOH, ethanol and a mixture of NaOH and ethanol – NaOH/ $\text{CH}_3\text{CH}_2\text{OH}$). Thermodynamic parameters were also determined to help explain the adsorption and desorption mechanisms involved. The main conclusions can be summarized as follows:

- The affinity of adsorption of the compounds for the carbon F400 was in the following order: nitrobenzene > isoproturon > phenol > clopyralid > metaldehyde. The comparative affinity was related to the aqueous solubility and hydrophobicity (represented by the $\log k_{\text{ow}}$ value) of the compounds.
- RO water was unable to achieve any significant desorption (<5%) of the compounds at room temperature, while greater desorption was evident at higher temperatures for phenol ($\sim 24\%$ at 80 °C) and clopyralid ($\sim 14\%$ at 80 °C). These findings indicated the existence of stronger interactions between the target contaminants and GAC, than might be explained by physisorption only.
- With the exception of phenol, strong solutions of NaOH (<2 M) were unable to achieve any significant desorption (<5%) of the other four compounds. For phenol, a DE of 40–50% was evident for a wide range of NaOH concentrations (0.1–2 M). This was partly attributed to the transformation of phenol to the phenolate ion and electrostatic charge repulsion from the negatively charged carbon surface.
- The hydrophobicity of the target contaminant was observed to influence the effectiveness of ethanol as a regenerant solution. Ethanol effectively desorbed phenol ($\sim 60\%$), nitrobenzene (35–45%) and isoproturon (40–70%), which are readily soluble in alcohol owing to their hydrophobicity.



• The NaOH/CH₃CH₂OH mixture was generally effective in desorbing all of the target contaminants due to the aggressiveness of ethoxide. Ethoxide interacts with the surface functional groups of the carbon and weakens the interactions between the adsorbed contaminants and the GAC, causing them to desorb.

• The NaOH/CH₃CH₂OH mixture did not transform or react with the target contaminants, except phenol, indicating that desorption process was governed by changes in the carbon surface properties.

• The results of calorimetry suggested that the selected contaminants, phenol, isoproturon and metaldehyde, adsorbed at two binding sites: a relatively weak binding site (site 1) where the contaminants are physisorbed to the carbon, and a second site (site 2) where a dynamic equilibrium occurs, and the contaminants bind with the carbon under chemisorption-like interactions, as indicated by a high energy of adsorption.

This study has demonstrated that a combined NaOH/CH₃CH₂OH solution was effective as a chemical regenerant by achieving the substantial desorption of a range of organic contaminants. Future research will consider the performance of repeated adsorption/desorption cycles in column tests, and the possible effects of the regenerant solution on the GAC properties, in order to confirm the potential value of chemical regeneration as a means of increasing the GAC bed life prior to full thermal regeneration and carbon disposal.

Conflicts of interest

There are no conflicts to declare.

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