Sorption of Metaldehyde using granular activated carbon

Salvestrini S.<sup>1\*</sup>, Vanore P.<sup>1</sup>, Bogush A.<sup>2</sup>, Mayadevi S.<sup>3</sup>, Campos L.C.<sup>2</sup>

<sup>1</sup>Department of Environmental, Biological and Pharmaceutical Sciences and Technologies. Second University of Naples. Via Vivaldi 43, 81100, Caserta (Italy).

<sup>2</sup>Centre for Resource Efficiency & the Environment, Department of Civil, Environmental & Geomatic Engineering, University College London, Chadwick Building, Gower Street, London WC1E 6BT, UK

<sup>3</sup>CEPD Division, CSIR-National Chemical Laboratory, Pune, India

## Abstract

In this work the ability of granular activated carbon (GAC) to sorb metaldehyde was evaluated. The kinetic data could be described by an intra-particle diffusion model which indicated that the porosity of the sorbent strongly influenced the rate of sorption. The analysis of the equilibrium sorption data revealed that ionic strength and temperature did not play any significant role in the metaldehyde uptake. The sorption isotherms were successfully predicted by the Freundlich model. The GAC used in this paper exhibited a higher affinity and sorption capacity for metaldehyde with respect to other GACs studied in previous works, probably as a result of its higher specific surface area.

Keywords: Metaldehyde, granular activated carbon, sorption, environmental pollution, diffusioncontrolled sorption

## 1. Introduction

Metaldehyde is a cyclic tetramer of acetaldehyde commonly used as molluscicide in agriculture and domestic gardening to control slugs, snails and other gastropods. Because it is an environmental contaminant, its current maximum application rate is fixed to 700 g metaldehyde/ha/calendar year in the UK (The Metaldehyde Stewardship Group, 2013).

<sup>\*</sup> Author to whom all correspondence should be addressed: e-mail: stefano.salvestrini@unina2.it; Phone: ++39(0)823274639Fax: ++39(0)823274605

Since 2008, the UK Environmental Agency has been reporting that metaldehyde level in drinking water exceeds European and UK limits of 0.1  $\mu$ g L<sup>-1</sup> (Busquets et al., 2014). This contaminant is inefficiently treated in water treatment plants. In fact, the maximum reported concentration of metaldehyde, in the UK water treated for drinking use is just above 1.03 ugL<sup>-1</sup> (Busquets et al., 2014).

There are different methods designed for reducing the concentration of metaldehyde in water (Tao and Fletcher, 2014; Tao and Fletcher, 2013; Busquets et al., 2014; Autin et al., 2012). An important method to reduce the concentration of metaldehyde is the photocatalytic degradation using UV/TiO<sub>2</sub> or UV/H<sub>2</sub>O<sub>2</sub> systems. Autin et al. (2012) showed that both UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> are able to efficiently degrade metaldehyde in pure systems. However, in natural waters, the UV/TiO<sub>2</sub> process is severely inhibited and the use of UV/H<sub>2</sub>O<sub>2</sub> remains the only reliable option for metaldehyde removal, although both these processes are relatively expensive compared to the conventional processes.

Among other techniques proposed for metaldehyde removal from water, sorption is the most interesting one because it is generally cheap and easy to scale up. Tao and Fletcher (2013) studied the sorption of metaldehyde onto three different materials:1) granular activated carbon (GAC): 2) non-functionalised hyper-cross-linked polymer; 3) ion-exchange resin. Their results indicated that the sorption kinetics of metaldehyde onto all tested materials was fast, reaching the equilibrium within 8 hours. They also showed that ion-exchange resin exhibited the highest sorption capacity (1807 mg g<sup>-1</sup>) and GAC was relatively inefficiencient in removing metaldehyde (71mg g<sup>-1</sup>). In terms of operational costs, ion-exchange resins are generally slightly cheaper than GAC (Griffin, 2009). However, on the other hand, GAC is less selective and hence more capable of adsorbing different types of pollutants.

The aim of this work is to investigate the sorption of metaldehyde onto a different commercial granular activated carbon by varying amount of the GAC, initial solute concentration, pH, ionic strength and temperature.

#### 2. Materials and methods

#### 2.1 Materials and reagents

Metaldehyde (CAS 9002-91-9) was supplied by Sigma-Aldrich; its main characteristics are reported in Table 1.

Metaldehyde	
Molecular formula	C <sub>8</sub> H <sub>16</sub> O <sub>4</sub>
Molecular mass	176.21 g/mol
Water solubility (25 °C)	213 mgL <sup>-1(1)</sup>
Appearance	White or colourless crystalline solid
Toxicity	Moderately toxic, kidney and liver toxicant <sup>(1)</sup>

Table 1. Main physicochemical characteristics of metaldehyde

(1) University of Herfordshire, Pesticide Properties Database-Metaldehyde, UK, 2012

The cartridges, styrene-divinylbenzene (SDB1) used for the solid phase extraction were provided by J.T.Baker while analytical (HPLC) grade methanol (CAS 67-56-1) and dichloromethane (CAS 75-09-2) were purchased from Fisher Scientific.

The coal based GAC used in this study was obtained from the Chemviron Carbon in the UK and used as received. The GAC particle size ranged from 1 to 2 mm. The BET surface area of the GAC is 774 m<sup>2</sup>/g. The GAC particle morphology with element analysis using SEM/EDS is presented in Figure 1. The GAC particles have a porous surface with a pore size < 200  $\mu$ m. The GAC mainly consists of C with impurities of Ca, Al, Si, and S.



Figure 1. Morphology and element analysis of the GAC particle.

# 2.2 Kinetics and sorption of metaldehyde

Metaldehyde sorption was studied by batch method. Kinetic experiments were performed by adding 10 mg of GAC to 100 mL of metaldehyde solution (30 mg L<sup>-1</sup>). The samples were agitated in a shaker (30 rpm) at room temperature and, at pre-decided contact times, 0.2 mL aliquots of reacting solution were removed for GC-MS analysis.

Metaldehyde sorption at equilibrium was studied by contacting 1-10 mg of GAC with 10 mL of metaldehyde solution (1-30 mg L<sup>-1</sup>). The samples were stirred at 30 rpm until the attainment of equilibrium and analyzed as described above. Sorption was studied as a function of temperature (5, 25, 45°C), pH (2-8) and ionic strength (0-1 M). The pH of samples was adjusted to the desired value with few drops of concentrated HCl or NaOH. KCl was used to alter the ionic strength of the solution.

# 2.3 GC-MS Analysis

Before GC-MS analysis, aliquots collected from the samples were pre-concentrated using solid phase extraction (SPE) according to the following procedure. A styrene-divinylbenzene (SDB1) cartridge was first activated flushing 10mL of methanol and then conditioned with 2mL of Mill-Q water. Afterwards, 0.2 mL of sample was passed through the cartridge. The cartridge was then

rinsed with 2 mL of Mill-Q water (to ensure that metaldehyde was entirely retained on the polymer) and dried by passing air through it for 40 min. Finally, the cartridge was flushed with 3 mL of dichloromethane; the fraction was collected in an appropriate glass tube and evaporated to 1 mL by nitrogen for GC-MS analysis. The GC-MS equipment used was a Perkin Elmer Clarus 500 which include an auto-injector, mass-spectrometer capable, a selective ion monitoring (SIM) mode (with a data solution), and a column HP5-MS (30 m×0.25 mm diameter, 0.25µm film thickness).

The injection model was split-less and the temperatures of injector and detector was set at 100°C and 180°C, respectively. Helium was used as carrier gas (1 mL min<sup>-1</sup>). The temperature programme for the oven was set at 100°C and hold for 1 min; then increase to 150°C at a rate of 5°C min<sup>-1</sup> and hold for 1 min.

## 3. Results and discussion

### 3.1 Sorption kinetics

A first attempt to model the sorption kinetic data was carried out using a pseudo-first and pseudosecond order equations.

According to the pseudo-first model (Lagergren, 1989), the sorption rate is proportional to the difference of the amount sorbed at equilibrium ( $q_e$ ,  $\mu g g^{-1}$ ) and at time t ( $q_t$ ,  $\mu g g^{-1}$ ):

$$\frac{\mathbf{d}\mathbf{q}_{t}}{\mathbf{d}t} = \mathbf{k}_{1}(\mathbf{q}_{e} \cdot \mathbf{q}_{t}) \tag{1}$$

where  $k_1$  (h<sup>-1</sup>) represents the pseudo-first kinetic rate constant.

Integrating Eq. (1) with the boundary conditions  $q_t = 0$  at t = 0 and  $q_t = t$  at t = t leads to:

$$q_t = q_e \left( 1 - e^{-\kappa_1 t} \right) \tag{2}$$

The pseudo-second order kinetics (Ho and Mackay, 1998) in its differential form is given by:

$$\frac{dq_t}{d_t} = k_2 (q_e - q_t)^2 \tag{3}$$

It can be integrated to give:

$$q_t = \frac{k_2 t q_e^2}{1 + k_2 t q_e} \tag{4}$$

where  $k_2$  (µg g<sup>-1</sup> h<sup>-1</sup>) is the pseudo-second order kinetic rate constant.

Figures 2 and 3 show the experimental kinetic data modelled according to the pseudo-first and pseudo-second equation, respectively. The equilibrium was achieved within about 48 h. The experimental data were better described by the pseudo-second order equation, as inferred by the higher correlation coefficient  $R^2$  and by the lower parameter errors (see Table 2).



Fig. 2. Pseudo-first order kinetic model for metaldehyde sorption



Fig. 3. Pseudo-second order kinetic model for metaldehyde sorption

Model	qe	<b>k</b> 1	<b>k</b> <sub>2</sub>	Z	kD	Ι	<b>R</b> <sup>2</sup>
	(µg g <sup>-1</sup> )	( <b>h</b> -1)	(g µg <sup>-1</sup> h <sup>-1</sup> )	( <b>h</b> -1)	(µg g <sup>-1</sup> h <sup>-0.5</sup> )	(µg g <sup>-1</sup> )	
Pseudo-first	(1.45±0.05)	0.45					0.870
order model	$\times 10^5$	$\pm 0.05$					
Pseudo-second	$(1.49 \pm 0.03)$		(4.8±0.5)				0.950
order model	$\times 10^5$		×10 <sup>-6</sup>				
Vermeulen	$(1.48 \pm 0.02)$			0.18±			0.975
model	$\times 10^5$			0.01			
Weber-Morris					(3.5±0.2)	(3.0±0.3)	0.965
model					$\times 10^4$	$\times 10^4$	

Table 2. Kinetic parameters for metaldehyde sorption as determined by the fitting procedure.

In order to confirm that the pseudo-second order equation was appropriate for describing the experimental data, the linearized form of this model as a control tool was examined.

The most used linearized form of eq. 4 is following (Mobasherpour et al., 2014; Vidal et al., 2011):

$$\frac{t}{q_t} = \frac{1}{k_2 q_g^2} + \frac{t}{q_g} \tag{5}$$

If the data obey to the pseudo-second order model, a plot of t/q vs t should produce a straight line. This is consistent with the results reported in Fig 4a.

However, it has been demonstrated (Canzano et al., 2012) that the use of eq. (5) may lead to incorrect conclusions, especially when the sorption data are at equilibrium (or very close to) because in such cases the plot t/q vs t becomes linear irrespective of the sorption kinetics.

(6)

A better option for reporting the experimental data may be to use the following linearized form:

$$\frac{q}{t} = k_2 q_e^2 - k_2 q_e q_t$$

The results using this model are presented in Fig 4b.



Fig. 4. Plots of metaldehyde kinetic sorption data: a) t/q vs t plot; b) q/t vs t plot

It can be seen from Figure 4b, that the data significantly deviate from linearity, especially at higher sorption amounts. This fact clearly suggests that the pseudo-second order model does not exhaustively describe the experimental data trend. This could be explained by the fact that the rate of sorption of metaldehyde onto GAC may be controlled by diffusion. In support of this hypothesis, it should be noted that GAC has a microporous structure (Figure 1) which could offer a resistance (via intra-particle diffusion) to the mass transfer of metaldehyde and, hence, limit the overall

reaction rate. Under this hypothesis and assuming that the sorbent particles are uniform and spherical and that the solute uptake is small relative to the total quantity introduced into the system, the sorption rate can be described by (Ruthven, 1984):

$$\frac{q_t}{q_{\infty}} = 1 - \frac{6}{\pi^2} \sum \exp\left(-\frac{D_c \pi^2 t}{r_c^2}\right) \tag{7}$$

where  $D_c$  (m<sup>2</sup> h<sup>-1</sup>) and r<sub>c</sub> (m) are intracrystalline diffusivity and mean radius of the sorbent particle respectively.

If the  $q_t/q_e$  ratio is > 0.1, the Vermeulen approximation can be applied (Inglezakis and Poulopoulos, 2006) so that eq. (7) reduces to:

$$q_t = q_e \sqrt{1 - exp(-Zt)} \tag{8}$$

where Z (h<sup>-1</sup>) is  $D_c \pi^2 / r_c^2$ .

The above equation was used to model the experimental kinetic data and the results are reported in Fig. 5 and Table 2. It can be seen that eq. (8) gives better fit as compared to the pseudo-first and pseudo-second order model both in terms of  $R^2$  and parameter errors. This leads us to conclude that diffusion plays a major role in the sorption rate of metaldehyde onto GAC.



Fig.5. Vermeulen kinetic model for metaldehyde sorption.

The results of our study indicate that the uptake of metaldehyde takes place slowly compared to that measured using a different commercial GAC (henceforth GAC-2; Tao and Fletcher, 2013). For our GAC, the time required to reach equilibrium was about 24 h (Fig. 5), whereas GAC-2, had shorter (about 6 h) equilibration time. Having assumed that diffusion controls the rate of sorption, it is

reasonable to ascribe the different behaviour of the two compared sorbents to their particle size as the rate of the process, in that case, should vary inversely with particle size (Boyd et al., 1947). Consistently with the results of the kinetic experiments, GAC used in the present work has greater particle size (1-2 mm) than that of GAC-2 (0.4-0.8 mm).

In order to strengthen the hypothesis that metaldehyde uptake is diffusion-controlled, initial sorption data (i.e. far from equilibrium) should be proportional to the square root of time according to the further simplification of eq. (7) derived by Weber-Morris (Weber and Morris, 1963; Salvestrini et al., 2014):

$$q_s = k_D \sqrt{t} + I \tag{9}$$

where  $k_D$  (µg g<sup>-1</sup> h<sup>-0.5</sup>) is the kinetic intra-particle diffusion constant and *I* (µg g<sup>-1</sup>) a constant proportional to the thickness of the boundary layer.

Therefore, a plot of q vs  $t^{0.5}$  should yield a straight line with slope and intercept with q axis equal to  $k_D$  and *I*, respectively. Fig 6 shows the Weber-Morris plot for the metaldehyde uptake onto GAC. The plot shows a good linearity in the range of time selected, thus confirming that, in the sorption process, intra-particle diffusion is the rate-limiting step.



Fig. 6. Weber-Morris plot for metaldehyde sorption

#### 3.2 Sorption Isotherms

The equilibrium data of metaldehyde sorption onto GAC were modelled using Langmuir, Freundlich and Langmuir-Freundlich models (Eq. 10, Eq. 11 and Eq. 12, respectively):

$$q_{e} = \frac{q_{max}k_{L}C_{e}}{1+k_{L}C_{e}} \tag{10}$$

$$q_{\varepsilon} = k_F C_{\varepsilon}^N \tag{11}$$

$$q_e = \frac{q_{max} K_{LF} C^N}{1 + K_{LF} C^N} \tag{12}$$

where  $q_e$  is the amount of the sorbate at the equilibrium,  $K_L$  (L µg<sup>-1</sup>),  $K_F$  (mg<sup>1-N</sup> g<sup>-1</sup> L<sup>N</sup>) and  $K_{LF}$  (L<sup>N</sup> µg<sup>-N</sup>) are the sorption affinity constants,  $q_{max}$  is the amount of sorbate necessary to complete a monolayer and *N* is a dimensionless constant related to the heterogeneity of the sorbent.

Figures 7 and 8 show the experimental data fitted with the Langmuir and Freundlich models, respectively. Metaldehyde sorption onto GAC was better described by the Freundlich model, especially at low solute concentration. These findings suggest the GAC behaves as heterogeneous material consisting of sorption sites which are not energetically equivalent (Toth, 2002).

Having established that the Langmuir model is not suitable to represent the sorption data, we used the Langmuir-Freundlich model in order to gain information on the saturation level of the sorbent.

Based on the results of the fitting procedure (Fig. 9 and Table 3), GAC has a  $q_{max}$  value of 320 mg g<sup>-1</sup>. It is worth noting that the value of  $q_{max}$  calculated in this work, is much higher than the value of 71 mg g<sup>-1</sup> (Tao and Fletcher, 2013) and 15 mg g<sup>-1</sup> (Busquets et al., 2014) obtained using other GACs. This is likely to be associated with the higher specific surface area of the GAC used for our experiments (774 m<sup>2</sup> g<sup>-1</sup>) compared to that used in the earlier studies (560 m<sup>2</sup> g<sup>-1</sup> and 500 m<sup>2</sup> g<sup>-1</sup>, respectively). Moreover, the sorbent used here has a higher affinity for metaldehyde, as the initial slope of its isotherm greater than that of the other GACs.

As mentioned in the introduction section, one of the main issues is the inefficiency of water treatment plants for reducing the metaldehyde concentration below the European limits of 0.1  $\mu$ g L<sup>-1</sup> (Busquets et al., 2014). Based on our results and considering that the treatment plant effluents may contain up to 1.03  $\mu$ g L<sup>-1</sup> of metaldehyde (Busquets et al., 2014), we can estimate that each gram of GAC would be sufficient to treat in batch reactors about 17,000 L of waste water so as to bring the concentration below the legal limit.

Model	KL	K <sub>F</sub>	K <sub>LF</sub>	Ν	q <sub>max</sub>	<b>R</b> <sup>2</sup>
	(L mg <sup>-1</sup> )	$(mg^{1-N} g^{-1} L^N)$	$(L^{N} mg^{-N})$		(mg g <sup>-1</sup> )	
Langmuir	270±30				220±10	0.962
isotherm						
Freundlich		1800±30		0.51		0.989
isotherm				±0.10		
Langmuir-Freundlich			(1.7±0.4)×	0.69	(320±70)	0.980
isotherm			10-3	±0.06		

**Table 3.** Thermodynamic parameters as determined by the fitting procedure.



Fig. 7. Langmuir isotherm for metaldehyde sorption.



Fig. 8. Freundlich isotherm for metaldehyde sorption.



Fig. 9. Langmuir-Freundlich isotherm of metaldehyde sorption.

### 3.3 Effect of pH, ionic strength and initial concentration

In order to investigate the effect of pH on the sorption of metaldehyde onto GAC, we carried out some experiments by varying pH in the range of 2-8. The results reported in Fig. 10, indicate that pH has no significant influence on the sorption of metaldehyde onto GAC. Notably, a few experiments carried out in water at pH = 2 revealed that metaldehyde is fully hydrolyzed to acetaldehyde, in agreement with previous findings (Booze & Oehme, 1986). This indicates that the presence of GAC has an inhibitory effect on the acidic hydrolysis of metaldehyde.



Fig 10. Effect of pH on metaldehyde equilibrium concentration.

The results of the sorption experiments obtained by varying the initial solute concentration ( $C_0$ ) are showed in Fig 11. As expected, the removal efficiency decreased with increasing  $C_0$ . In particular, the removal efficiency was very high (91%) at the lowest dose tested (1 ppm), whereas it decreased significantly up to 68% when  $C_0$  was 25 ppm.



Fig. 11. Effect of the initial liquid phase concentration on metaldehyde sorption.

To understand the effect of ionic strength, we examined the sorption performance of GAC in the presence of KCl. The sorption isotherms (not shown), within the experimental errors, were quite similar in the range of concentration explored (0M-1M). Therefore, ionic strength has no influence on the sorption process.

Likewise, also the temperature has no detectable influence on the sorption isotherms ( $\Delta H^{\circ} \approx 0$ ), hence suggesting that sorption is physisorption (Colella et al., 2015).

## 4. Conclusions

In the present work the sorption of metaldehyde onto granular activated carbon was investigated. It was found that GAC has an energetically heterogeneous surface. The rate of the sorption is diffusion-controlled. Among different models tested, the hybrid Freundlich isotherm was found to describe more adequately the sorption data at equilibrium, whereas the Vermeulen equation was found to be appropriate for modelling kinetic data indicating that the process is rate limited by intraparticle diffusion. Ionic strength, pH and temperature have no significant influence on metaldehyde uptake.

## Acknowledgments

The authors are thankful to Dr. Judith Zhou and Dr Catherine Unsworth of the Department of Civil, Environmental and Geomatic Engineering at University College London, for their precious technical support. Part of this study was supported by the DST-UKIERI Thematic Partnerships (DST-2013-14/080).

#### References

- Autin, O., Hart, J., Jarvis, P., MacAdam, J., Parsons, S.A., Jefferson, B., 2012.Comparison of UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> for the degradation of metaldehyde: kinetics and the impact of background organics. Water Research 46, 5655-5662.
- Booze, T.F. and Oehme, F.W., 1986. An Investigation of Metaldehyde and Acetaldehyde Toxicities in Dogs. Applied Toxicology 6, 440-446.
- Boyd, G., Adamson, A., Myers, Jr. L., 1947. The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics. Journal of American Chemical Society 69, 2836– 2848.
- Busquets, R., Kozynchenko, O.P., Whitby, R.L.D., Tennison, S.R., Cundy, A.B., 2014. Phenolic carbon tailored for the removal of polar organic contaminants from water: A solution to the metaldehyde problem?. Water Research 61, 46-56.
- Canzano, S., Iovino, P., Leone, V., Salvestrini, S., Capasso, S., 2012. Use and Misuse of Sorption Kinetic Data: A Common Mistake that Should be Avoided. Adsorption Science e Technology 30 (3), 217-226.
- Colella, A., de Gennaro, B., Salvestrini, S., Colella, C., 2015. Surface interaction of humic acids with natural and synthetic phillipsite. Journal of Porous Materials 22, 501–509.
- Ho, Y.S., McKay, G., 1998. Sorption of dye from aqueous solution by peat. Chemical Engineering Journal 70, 115- 124.
- Griffin, R.D., 2009. In: Principles of Hazardous Materials Management. ISBN-13: 978-1420089707, CRC Press, 2009
- Lagergren, S., 1989. Zur theorie der sogenannten adsorption gelster stoffe. Handlingar 24, 1-39.
- Mobasherpour, I., Salahi, E., Ebrahimi, M., 2014. Thermodynamics and kinetics of adsorption of Cu(II) from aqueous solutions onto multi-walled carbon nanotubes. Journal of Saudi Chemical Society 18 (6), 792–801.
- Poulopoulos, S., Inglezakis, V., 2006. In: Adsorption, Ion Exchange and Catalysis: Design of Operations and Environmental Applications. Elsevier .
- Ruthven, D.M., 1984. In: Principles of Adsorption and Adsorption Processes, John Wiley and Sons.

- Salvestrini, S., Leone, V., Iovino, P. Canzano, S., Capasso, S., 2014. Considerations about the correct evaluation of sorption thermodynamic parameters from equilibrium isotherms. Journal of Chemistry Thermodynamics, 68, 310- 316.
- Tao, B., Fletcher, A.J., 2013. Metaldehyde removal from aqueous solution by adsorption and ion exchange mechanisms onto activated carbon and polymeric sorbents. Journal of Hazardous Materials 244–245, 240-250.
- Tao, B., Fletcher, A.J., 2014. Catalytic degradation and adsorption of metaldehyde from drinking water by functionalized mesoporous silicas and ion-exchange resin. Separation and Purification Technology 124, 195-200.
- The Metaldehyde Stewardship Group, 2013. Promoting Responsible Metaldehyde Applications http://www.getpelletwise.co.uk/news/archive/700g\_metaldehyde\_now\_legal\_max\_/
- Toth, J., 2002. In: Adsorption. Theory, modelling and analysis. CRC Press, 2002.
- Vidal, C.B., Barros, A.L., Moura, C.P., de Lima, A.C.A., Dias, F.S., Vasconcellos, L.C.G., Fechine, P.B.A., Nascimento, R.F., 2011. Adsorption of polycyclic aromatic hydrocarbons from aqueous solutions by modified periodic mesoporous organosilica. Journal of Colloid and Interface Science, 357 (2), 466–473.
- Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on carbon from solution. Journal of the Sanitary Engineering Division 89, 31-59.