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The oxidation of aqueous thiols on a graphite intercalation compound adsorbent

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Abstract Aqueous phase adsorption of thiols onto a graphite intercalation compound (GIC) adsorbent was shown to be accompanied by surface assisted oxidation of the thiols to their disulfide dimer. This effect was studied for three thiols; ethanethiol, propanethiol and sec-butanethiol. Unlike the case of thiol oxidation on activated carbons in aqueous conditions, the generation of dimer did not affect the adsorbent's ability to oxidise the thiols in solution in the concentration range studied (0–100 ppm). This was attributed to the non-porous, crystalline nature of the adsorbent. This meant that once formed the dimers migrated from the active sites for thiol oxidation, believed to be mainly at the edges of the graphite planes, onto the hydrophobic basal plane where they could be adsorbed. Oxidation of the GIC adsorbent in the anodic compartment of an electrochemical cell was shown to attenuate the adsorbent's ability to oxidise thiols. It was inferred that this was a result of a decrease in the amount of CO groups at the plane edges caused by this oxidation process.

Keywords Adsorption · Oxidation · Graphite · Mercaptans

1 Introduction

The removal of organic sulfur compounds from waste streams presents a challenge shared across several industries including the pulp and paper, petroleum refining and waste water treatment industries (Rios et al. 2008). The disagreeable odour of these compounds, which can be a nuisance at concentrations as low as ppb level (Smet and Langenhove 1998), means that wastes in both liquid and gas form have to be controlled at source. Different industries use different techniques to remove these components depending on effluent characteristics such as concentration, volume and required discharge consent (Rafson 1998). Activated carbons are considered a best available technique (BAT) and are used to remove these components by adsorption (Bashkova et al. 2002a). An interesting feature of the removal of thiols using activated carbon is the oxidation of adsorbed thiols to disulfides, a more readily adsorbed hence removed species (Bashkova et al. 2002a).

In this paper the ability of a non-porous, electrically conducting graphite intercalation compound (GIC) to adsorb and oxidise thiols is studied. GICs have recently been used as adsorbents in a number of water and gas treatment processes based on fast adsorption coupled with adsorbent regeneration (Conti-Ramsden et al. 2012b; Mohammed et al. 2011; Brown and Roberts 2007; Brown et al. 2004a, b). In these processes electrochemical oxidation is used to restore the adsorbent's adsorptive capacity by anodic oxidation in an electrochemical cell. Combining adsorption and regeneration results in a series of process advantages such as in-situ adsorbent regeneration, energy efficient organic oxidation and no secondary waste stream to be treated (Mohammed et al. 2011). One application currently under investigation is the removal of odour from aqueous effluent and waste water treatment plant (WWTP) off-gas (Conti-Ramsden et al. 2012c). During experimentation oxidation of adsorbed thiols by the GIC adsorbent was observed. Thiol oxidation to disulfide has been shown by other authors to give abatement advantages to

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adsorption processes (Bashkova et al. 2002a; Katoh et al. 1995) so this phenomena was investigated to elucidate any advantages that it might have for the adsorption-regeneration process being developed. The oxidation of thiols on GIC surfaces has not been previously recorded in the literature but the oxidising properties of GICs as a result of the intercalation process are documented (Armand and Touzain 1977). Parallels between the oxidative characteristics of GICs and that observed on the surface of graphene oxides (GO) (Dreyer et al. 2011, 2010a) can be drawn as GICs exhibit properties somewhere between graphite and GO (Dreyer et al. 2010b; Ishikawa et al. 1978).

Literature does exist on thiol oxidation on activated carbon surfaces. Researchers reported that methyl mercaptan (MM), a widely studied thiol, can be adsorbed by activated carbon at room temperature in its porous structure (Bashkova et al. 2002a; Bagreev et al. 2002). In the presence of oxygen, oxidation of the MM occurs in these pores and can produce a variety of oxidation products, the most prevalent being dimethyl disulphide (DMDS) (Bashkova et al. 2002a). This effect has also been observed for other sulfur compounds such as hydrogen sulfide and propanethiol (Bashkova et al. 2002a; Meeyoo and Trimm 1997; Katoh et al. 1995). This effect is significant as the oxidation product tends to be more readily adsorbed. The nature of room temperature adsorption and oxidation of thiols on activated carbon has been shown by several authors to depend on: the presence of water in which thiol dissociation and dissolved oxygen are key in a proposed “Island Mechanism” (Bashkova et al. 2002a; Katoh et al. 1995); the surface chemistry and porous nature of the activated carbon (Rios et al. 2008; Meeyoo and Trimm 1997), particularly pH (Bashkova and Bandosz 2005; Bashkova et al. 2002b), and the nature of minerals present in the activated carbon such as iron which has been shown to perform a catalytic role in the oxidation of MM to DMDS (Bashkova and Bandosz 2005).

Where carbon is oxidising as well as adsorbing, component removal from the mobile phase continues until adsorbent capacity exhaustion and the exhaustion of the surface oxidising species or poisoning of the oxidation mechanism. Poisoning can occur as a result of reaction product species or other species competing for active sites. In the presence of oxygen, the bulk of the literature on gas phase adsorption of MM agrees that the main poisoning mechanism involves the adsorption of DMDS on active sites. DMDS is adsorbed more strongly than MM due to its size and boiling point and is also likely to replace adsorbed water due to its lower solubility in water (Bashkova et al. 2002a; Bagreev et al. 2002; Meeyoo and Trimm 1997). By using *n*-hexene as the liquid phase so DMDS was no longer adsorbed preferentially, Rios et al. (2008) demonstrated that there was a further limiting factor to surface oxidation on carbons. The authors postulated that the depletion of specific oxidation containing surface groups, most likely to be quinones, limited thiol oxidation after having ruled out the effect of dissolved oxygen.

This paper will investigate the adsorption and oxidation of thiols on GIC adsorbents in the context of the adsorption-regeneration process described in earlier work (Conti-Ramsden et al. 2012a, c). Where Conti-Ramsden et al.’s paper (2012a) indicated that there might be oxidation occurring on the GIC surface this paper attempts to understand the surface effects in more detail.

2 Experimental

2.1 Adsorbent and adsorbate

Nyex 1000 is a GIC adsorbent material. It is supplied as flakes with a mean particle diameter of 500 μm. Nyex 1000 is non-porous (Fig. 1) and has no internal surface area (demonstrated by mercury porosimetry). As a result of its non-porous surface it demonstrates fast adsorption kinetics (adsorption equilibrium time of the order of minutes (Brown et al. 2004a)) as there is no diffusion dependent adsorption. The BET surface area of the particles has been determined by nitrogen adsorption and was found to be 0.8 $m^2\ g^{-1}$. This is low when compared with more conventional adsorbents such as activated carbon whose surface area may range from 600 to 2,500 $m^2\ g^{-1}$. The non porous, graphitic nature of the Nyex also results in the material being dense, with a particle density of 2.2 gcm^{-3}, and able to conduct electricity. The measured packed bed electrical conductivity is $\sim$0.8 Scm^{-1}. Nyex is acidic and was shown by elemental analysis to consist mainly of carbon, oxygen and sulfur with some other trace components. The GIC adsorbent is crystalline in structure and effectively has two distinct adsorption sites. Previous work has demonstrated that the majority of reactive functional groups are expected at the exposed edges of graphene layers in graphitic activated carbons and that the flat basal planes consist mainly of hydrophobic graphene like sheets (Coughlin et al. 1968) with defects. This is consistent with a model that would describe GICs as somewhere between graphite and graphite oxide (Dreyer et al. 2010b; Ishikawa et al. 1978) as the GIC adsorbent shows some oxygen functionality on the basal planes. The thiols studied, ethanethiol, propanethiol and sec-butanethiol and their corresponding disulfides were supplied in liquid form as analytical grade by Sigma Aldrich with a purity of 98 %. All other chemicals were supplied as analytical grade by Sigma Aldrich. Nyex 1000 was supplied by Arvia Technology Ltd. in the form of flakes and will be referred to as “the GIC adsorbent” in this paper.

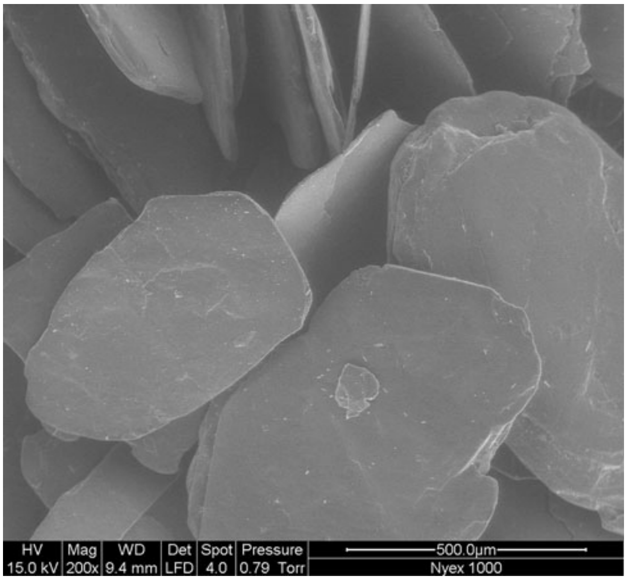

Fig. 1 SEM picture of the GIC adsorbent used in this study taken at ×200 magnification showing the flake particle morphology

2.2 Analytical techniques

Ambient temperature headspace analysis (Agilent 7694 E headspace sampler) was used to sample volatile species in 20 ml sealed vials containing 15 ml of liquid sample. Sample analysis was conducted by gas chromatography (GC, Agilent 6890 N) with a flame ionisation detector (FID). Non-volatile component sampling and analysis was conducted by direct liquid injection of a filtered sample into the GC-FID. The GC operating parameters can be found in Table 1. The GC methods used were as follows: ethanethiol, 160 °C for 3.5 min, propanethiol, 160 °C for 5 min and 2-butanethiol, 210 °C for 3.7 min. Mixtures were analysed by a method which held the column at 90 °C for 5 min and then ramped up to 210 °C at a rate of 30 °C per minute. The column was then allowed to cool to 90 °C before the next run. EDAX (FEI Quanta 200 ESEM) was used to determine the elemental composition of the GIC particles. A total of 50 particles were analysed and an average elemental content taken for each species on both the basal planes and the edge surfaces.

2.3 Adsorption/oxidation experiments

To study the rate of oxidation of the thiols in conditions representative of the adsorption-regeneration process 15 ml of a 100 ppm aqueous thiol solution was sealed in a 20 ml headspace vial with a known amount of the GIC adsorbent. Several such assays were prepared so that the removal and breakdown product profile could be determined over time. These were performed next to a series of blanks containing inert PTFE beads. The samples were mixed on a Heidolph orbital shaker at 200 rpm and all experiments were conducted at ambient temperature (22 °C). To determine if the observed oxidation was related to the oxygen available in the reaction environment tests were carried out in anoxic conditions. Water was purged with nitrogen for 30 min before the addition of thiol and the GIC adsorbent in a sealed 20 ml vial filled completely so as to eliminate any headspace. Liquid phase thiol and disulfide analysis was then conducted by liquid injection GC-FID.

To assess the effect of any active site blockage by dimer on the rate of oxidation a series of experiments were conducted in which an excess of disulfide (100 ppm) was added to an assay containing a known mass of the GIC adsorbent and 100 ppm of thiol. The concentration of the thiol was then monitored over time by the same method as used above.

2.4 Change in oxidative activity after anodic oxidation of the adsorbent

Adsorbent regeneration is key to the process of water treatment using GIC adsorbents (Conti-Ramsden et al. 2012c; Mohammed et al. 2011) hence behaviour of the GIC as an oxidant was assessed after electrochemical oxidation. The GIC adsorbent was oxidised in the anodic compartment of an electrochemical cell as used by Brown and Roberts (2007). The cell had an electrode area of ~65 cm^2, adsorbent bed thickness of 20 mm and the catholyte used was 0.3 % acidified brine [0.3 % (wt/wt) NaCl containing 0.025 M HCl]. The adsorbent was oxidised for different lengths of time at a current density of 20 mA cm^{-2} to vary the charge passed hence the oxidation state and surface functionality of the GIC adsorbent. The adsorbent was then washed and dried in an oven at 60 °C

Table 1 GC and headspace table of parameters employed

Parameters	Settings	GC	Settings
Vial Eq. time	0 min	Split ratio	1:1
Pressurisation time	0.3 min	Injector temp.	130 °C
Injection time	1 min	Inlet pressure	8.9 psi
Loop Eq. time	0.15 min	Total flow	4.0 ml min^{-1}
Loop fill time	0.2 min	FID temp.	250 °C
Transfer line temp.	120 °C	Column	ZB-1

for 24 h to remove any aqueous phase oxidising species. The adsorption/oxidation experiments were repeated with the regenerated GIC adsorbent to observe any difference in rate of oxidation. An elemental analysis of the GIC adsorbent was carried out to determine the adsorbent's oxygen content after oxidation for different time periods.

3 Results and discussion

3.1 Thiol adsorption and oxidation

Two phenomena were observed when the GIC adsorbent came into contact with the aqueous thiols, adsorption and oxidation. Figure 2 shows thiol concentration with time in 15 ml, 100 ppm thiol solutions containing 0.5 g of the GIC adsorbent. The decay in thiol concentration is a result of both adsorption and oxidation. Adsorption onto the GIC adsorbent has been shown to be a quick process in earlier work, with the bulk of adsorption (>88 %) occurring within 2 min (Brown et al. 2004b) and equilibrium achieved within 30 min. Looking at Fig. 2 it is possible to see fast thiol removal rates in the initial 10 min of the experiment followed by a slower decay in concentration with time. It is proposed that in the first 10 min, adsorption dominates thiol removal after which the bulk of the GIC adsorbent's adsorptive capacity is exhausted and another removal mechanism takes over. Past work on the importance of hydrophobicity in adsorption from aqueous solution (Moreno-Castilla 2004) together with the structure of GIC (Dreyer et al. 2010a) would suggest that adsorption is driven by the hydrophobic interaction onto the graphitic basal plane. A separate paper validating this assertion is currently under review. In Fig. 2 the effect of adsorption is clearest for the largest thiol studied, sec-butanethiol, consistent with it having the greatest affinity for the hydrophobic GIC adsorbent surface due to its size, boiling point and hydrophobicity when compared to the other thiols.

Subsequent thiol removal is attributed to the oxidation of the thiol to its disulfide form alongside either the reduction of dissolved oxygen, water or the GIC adsorbent itself. In all cases a secondary peak was detected alongside the primary thiol peak and confirmed to be the associated disulfide by comparing elution GC times to disulfide standards.

The disulfide concentration was also monitored with time for the above experiment and the results are shown in Fig. 3. Stoichiometrically two thiols are required per disulfide formed. As a result of the mass difference between the thiols and disulfides if 100 ppm of thiol is completely oxidised to the corresponding disulfide, ~100 ppm of the disulfide should be produced assuming no further reaction. Figure 3 demonstrates that, despite complete removal by adsorption and/or oxidation by the GIC in the case of all the thiols studied, different resulting disulfide concentrations are observed in solution. No further oxidation products were observed in solution. This suggests that the different disulfides formed have different adsorptive affinities to the GIC adsorbent and as a result, once formed, this affinity dictates how much of the breakdown product is released into solution. This is not surprising as the different disulfides are of different solubilities and hydrophobicities. The effect of disulfide on the oxidation of thiols is investigated in the section entitled 'effect of the dimer on thiol oxidation'.

The rate of thiol oxidation in the experimental conditions studied was shown to be first order with mass of the GIC adsorbent (Fig. 4). Mass transfer was very likely limiting the rate of oxidation due to the mixing regime used so no conclusions were drawn from the rate data other than

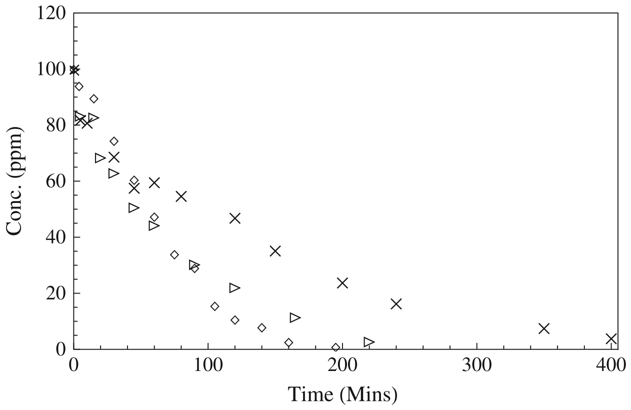

Fig. 2 Thiol concentration against time for 0.5 g of the GIC adsorbent contacted with 15 ml, 100 ppm thiol solutions in a sealed vial. Ethanethiol (*white diamond*), propanethiol (*white right pointing triangle*) and sec-butanethiol (*times*)

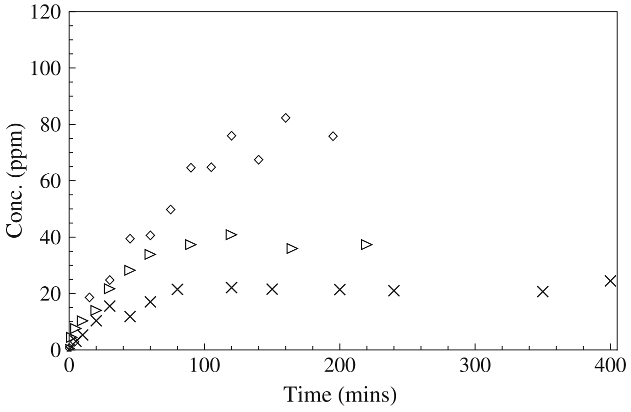

Fig. 3 Disulfide concentration against time for 0.5 g of the GIC adsorbent contacted with 15 ml, 100 ppm thiol solutions in a sealed vial. Ethyl-disulfide (*white diamond*), propyl disulfide (*white right pointing triangle*) and sec-butyl disulfide (*times*)

rate of oxidation appeared to be directly correlated with molecular diffusivity (Table 2) giving a fit better than $R^2 = 0.97$ when rate was plotted against diffusion coefficient in water.

Considering the oxidation mechanism, contacting the GIC adsorbent with thiols under anoxic conditions resulted in the same behaviour as observed when oxygen was freely available in the system in terms of both rate and completeness of oxidation. This confirmed that a mechanism akin to that observed by Rios et al. involving reducible surface functional groups was occurring (Rios et al. 2008) rather than iron and/or alkali facilitated oxidation of thiols with adsorbed oxygen as observed by Bashkova and Bandosz (2005) in the case of some activated carbons. This is also consistent with the surface group characterisation of the adsorbent studied as discussed in the elemental analysis.

3.2 Effect of the dimer on thiol oxidation

The solvent has been shown to have an important role in terms of preferential adsorption in the liquid phase as it strongly influences the nature of the competition for active sites (Rios et al. 2008; Bagreev et al. 2002). These effects are not only influenced by the nature of the solvent, but also by the nature of the breakdown products. To study the effect of the dimer on thiol oxidation the above adsorption/oxidation experiments were repeated but in this case the solvent was spiked with 100 ppm of the expected dimer. The results in Fig. 5 compare thiol removal in the case of both the spiked and un-spiked solvent and Fig. 6 shows the overall dimer concentration during the experiments. Figure 5 demonstrates that, despite the presence of the dimer, the rate of oxidation is only slightly reduced in all cases. Figure 6 again highlights the difference in disulfide adsorption affinity demonstrating that in the case of ethyl disulfide, a weaker interaction results in the overall concentration of disulfide increasing. This is in contrast with propyl disulfide and sec-butyl disulfide which appear to retain most of the disulfide produced by oxidation on the adsorbent surface.

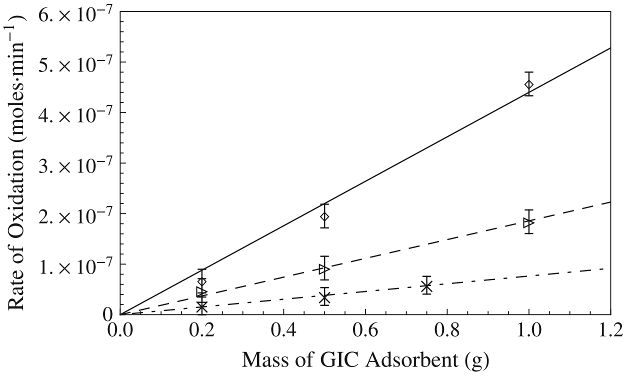

Fig. 4 Rate of oxidation of the challenge thiols against mass of the GIC adsorbent showing a first order relationship for the thiols: ethanethiol (*white diamond*), propanethiol (*white right pointing triangle*) and sec-butanethiol (*times*)

Table 2 Measured rate of thiol oxidation and thiol molecular diffusivities (Yaws 2012)

Compound	Rate of oxidation × 10^7 (moles · g^{-1} · min^{-1})	Diffusion coeff. (water) × 10^{-5}(cm^2 · s^{-1})
Ethanethiol	4.4	1.2
Propanethiol	1.9	1.0
2-Butanethiol	0.8	0.9

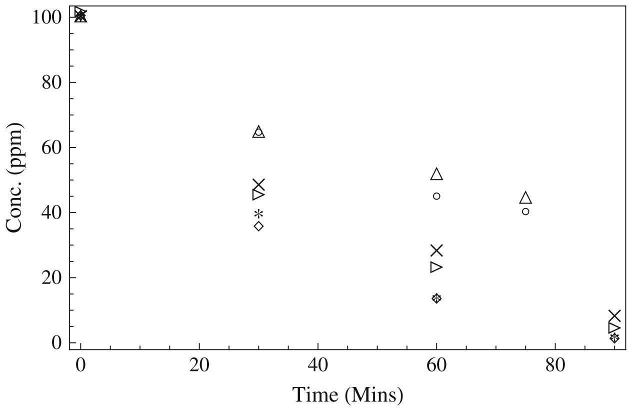

Fig. 5 Thiol concentration with time in 15 ml aqueous solutions containing0.5 g of the GIC absorbent and 100 ppm of thiol (ethanethiol(*white diamond*), propanethiol (*white right pointing triangle*), sec-butanethiol (*white circle*)). Also shown are thiol concentrationswith time in a 100 ppm thiol, 100 ppm disulfide aqueoussolution (ethanethiol and ethyl disulfide (*star*), propanethiol and propyldisulfide (*times*), sec-butanethiol and sec-butyl disulfide (*white triangle*))

The difference in disulfide affinities to the adsorbent together with the fact that in all cases the rate of oxidation is not affected by disulfide in the spectator solvent would suggest that, in contrast to activated carbons, the blocking of active sites on the GIC adsorbent does not appear to be a key mechanism for poisoning oxidation activity in the concentration ranges studied. This effect might be explained by the crystalline nature of the GIC adsorbent which has two distinct types of surface; a flat, hydrophobic carbon surface and broken graphene edges which contain the bulk of the GIC adsorbent's functionality, similar to that of a lower oxidation state graphite oxide surface (Jia et al. 2011). It could therefore be expected that the bulk of adsorption occurs on the hydrophobic basal surface and the bulk of component oxidation occurs at the functionalised graphene plane edges. The formation of the significantly more hydrophobic disulfide at the plane edges would

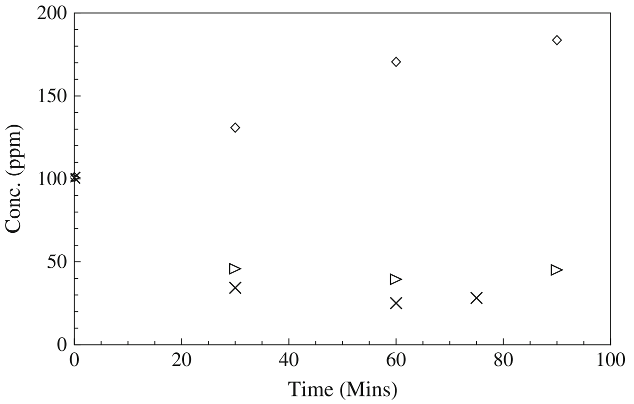

Fig. 6 Corresponding disulfide concentration in the 15 ml 100 ppm thiol, 100 ppm disulfide aqueous solutions containing 0.5 g of the GIC adsorbent shown in Fig. 5. Ethyl disulfide (*white diamond*), propyl disulfide (*white right pointing triangle*) and sec-butyl disulfide (*times*)

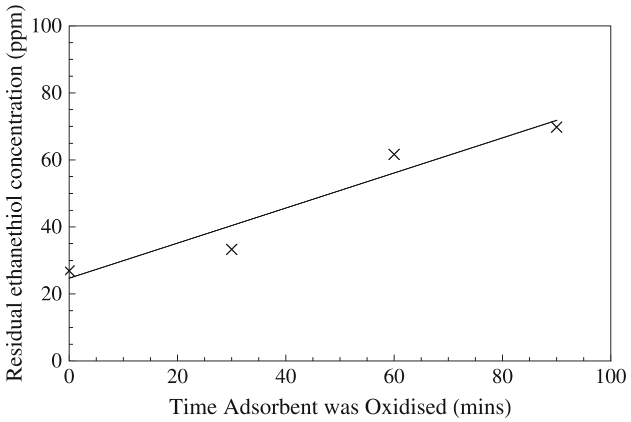

Fig. 7 Residual ethanethiol after 70 min of contact between 15 ml, 100 ppm aqueous solution of ethanethiol with 0.5 g of the GIC adsorbent which had undergone electrochemical oxidation for different times of 0, 30, 60 and 90 min at a current density of 20 mA cm^{-2}

promote component migration to the hydrophobic surface where the component would be adsorbed. Having a sink available for the hydrophobic disulfide could keep the active edges un-blocked hence mitigate the effect of disulfide production on the oxidation of thiols in solution. This is in contrast to adsorption on GAC in which poisoning by active site blocking is a key mechanism. Further work is necessary to test this hypothesis.

3.3 Changes in oxidative activity by anodic oxidation of the adsorbent

In the anodic compartment of an electrochemical cell the GIC is able to electrochemically oxidise adsorbed organics (Brown and Roberts 2007; Brown et al. 2004a). The adsorbent itself can also be electrochemically oxidised which changes surface oxygen content and functional group distribution, hence affecting the oxidative characteristics of the material. As the GIC adsorbent is designed for use in an adsorption-oxidation process, the effect of oxidation on the adsorbent's ability to oxidise thiols was tested. Fresh GIC adsorbent was oxidised in an electrochemical cell similar to that used by Brown and Roberts (2007) for differing lengths of time then subjected to adsorption-oxidation experiments.

Figure 7 shows the amount of thiol present after 70 min of contact between 15 ml, 100 pmm ethanethiol solutions and GIC adsorbent that had been anodically treated for different lengths of time at a current density of 20 mA cm^{-2}. Contact continued for more than 24 h and this time was found to be in-sufficient for the adsorbents treated for 60–90 min to fully remove or oxidise the thiol present.

This result suggested that the oxidation process reduced the oxidative characteristics of the GIC. Considering the GIC adsorbent to have graphite oxide-type properties, the oxidation observed would proceed by the direct oxidation of the thiol in tandem with direct reduction of the GIC adsorbent via a reduction of the graphene sheets in the structure. Modifying the equation developed by Zhou et al. 2009 to describe the GIC adsorbent oxidising the thiol and being itself reduced gives equation Fig. 1.

$$\mathrm{GIC} + 2\mathrm{RSH} \rightarrow \mathrm{Reduced\ GIC} + \mathrm{H_2O} + \mathrm{RSSR} \quad (1)$$

The above mechanism would suggest that the depletion of reducible oxygen surface groups on the adsorbent could be the limiting factor in the oxidation of thiols in the liquid affecting both rate and capacity to oxidise. Surface oxygen content was monitored on the GIC adsorbent by EDAX and followed on both the edges and on the basal plane. There was no clear correlation with basal plane oxygen content and oxidation time. However it was shown that the amount of oxygen increases on the active edges of the GIC with increasing charge passed (Table 3). This result was expected as oxidation of the adsorbent should result in increasing surface oxygen. The increase of surface oxygen content together with the decrease in oxidation rate would suggest, as in the case of activated carbon (Rios et al. 2008), that the oxidation is based on a specific type of surface oxygen group. Identification of the surface groups responsible for oxidation is very difficult for GIC's as it is not possible to use

Table 3 Elemental analysis by EDAX of the edges of the GIC adsorbent showing the oxygen content at different electrochemical treatment times

Treatment time	O content (%)
0	5.58
30	7.22
60	8.39
90	9.48

temperature programmed desorption (TPD) to determine the nature of the surface groups (usually characterised as CO or CO_2 evolving groups (Garcia-Oton et al. 2005)) as temperatures greater than 150 °C cause exfoliation of the GIC adsorbent (Herold et al. 1994), rendering the method unsuitable. Further, leaching of the acidic intercalant in the GIC interfered with attempts at Boehm titration which prevented the characterisation of the distribution of acidic/basic surface groups by this method. Method development to characterise the adsorbent is currently on-going but an indication of likely oxidising species can be determined from available literature on the anodic oxidation of carbons.

Work on the anodic oxidation of activated carbons saturated with toluene (Garcia-Oton et al. 2005) using TPD demonstrated that anodic treatment results in the overall increase of surface oxygen groups on the surface. However this increase is confined to those groups evolved as CO_2 with the content of groups evolved as CO shown to decrease. More recent work has demonstrated that at lower carbon oxidation levels the evolved CO/CO_2 ratio by TPD is relatively high, but this decays to a plateau as the oxidation state increases (Berenguer et al. 2012). Given the above trends in surface oxygen content and surface oxygen group type together with the results obtained in this study one can also conclude that, as in the study of thiol oxidation by activated carbons (Rios et al. 2008), it is likely that CO evolving groups are responsible for the oxidation of thiols on the GIC adsorbent. The most likely groups would be quinones which have been shown to readily oxidise thiols (Rios et al. 2007; Ishizaki and Cookson 1973). Further work is required to address the effect of oxidation on surface oxygen content and functional group distribution on the GIC adsorbent.

4 Conclusions

It was demonstrated that the studied non-porous, GIC adsorbent could oxidise thiols to disulfides on its surface. Unlike thiol oxidation on activated carbons in aqueous systems, disulfide formed by the oxidation process did not poison the oxidation process under the experimental conditions studied. This was attributed to the crystalline nature of the GIC adsorbent which has two types of surface: a hydrophobic basal plane and graphene plane edges which contain most of the oxygen functionality. It was proposed that the bulk of oxidation occurred on the functionalised graphene plane edges and that the majority of adsorption occurred on the hydrophobic basal planes. The affinity of the hydrophobic disulfide for the hydrophobic basal plane facilitates the transfer away from the active sites on the edge after oxidation which prevented the poisoning of thiol oxidation through active site blocking by the disulfide oxidation product.

It was also demonstrated that dissolved oxygen in the aqueous phase did not contribute to the observed oxidation by repeating experiments in an anoxic environment, hence the oxidation was attributed to oxygen containing surface functional groups. The distribution of oxygen containing functional groups was changed by oxidising the GIC adsorbent in the anodic compartment of an electrochemical cell. This form of oxidation has been shown to increase overall surface oxygen content but reduce the amount of oxygen functional groups evolved as CO under temperature programmed desorption analysis. Experiments demonstrated that the oxidised GIC adsorbent was not as effective at oxidising the thiols to their disulfide form hence oxygen functional groups of the CO type (probably quinones) were most likely responsible for the oxidation observed.

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References

Armand, M., Touzain, P.: Graphite intercalation compounds as cathode materials. Mater. Sci. Eng. **31**, 319–329 (1977)

Bagreev, A., Bashkova, S., Bandosz, T.J.: Dual role of water in the process of methyl mercaptan adsorption on activated carbons. Langmuir. **18**, 8553–8559 (2002)

Bashkova, S., Bandosz, T.J.: Catalytic properties of activated carbon surface in the process of adsorption/oxidation of methyl mercaptan. Catal Today **99**, 323–328 (2005)

Bashkova, S., Bagreev, A., Bandosz, T.J.: Adsorption of methyl mercaptan on activated carbons. Environ. Sci. Technol. **36**, 2777–2782 (2002a)

Bashkova, S., Bagreev, A., Bandosz, T.J.: Effect of surface characteristics on adsorption of methyl mercaptan on activated carbons. Ind. Eng. Chem. Res. **41**, 4346–4352 (2002b)

Berenguer, R., Marco-Lozar, J.P., Quijada, C., Cazorla-Amorós, D., Morallón, E.: A comparison between oxidation of activated carbon by electrochemical and chemical treatments. Carbon Balance. Manage. **50**, 1123–1134 (2012)

Brown, N.W., Roberts, E.P.L.: Electrochemical pre-treatment of effluents containing chlorinated compounds using an adsorbent. J. Appl. Electrochem. **37**, 1329–1335, doi:10.1016/S0009-2614(98)00144-4 (2007)

Brown, N.W., Roberts, E.P.L., Chasiotis, A., Cherdron, T., Sanghrajka, N.: Atrazine removal using adsorption and electrochemical regeneration. Water Res. **38**, 3067–3074 (2004a)

Brown, N.W., Roberts, E.P.L., Garforth, A.A., Dryfe, R.A.W.: Electrochemical regeneration of a carbon based adsorbent loaded with crystal violet dye. Electrochim. Acta. **49**, 3269–3281 (2004b)

Conti-Ramsden, M.G., Asghar, H.M.A., Hussain, S.N., Roberts, E.P.L., Brown, N.W.: Removal of mercaptans from a gas stream using continuous adsorption-regeneration. Water Sci. Technol. **66**(9), 1849–1855 (2012a)

Conti-Ramsden, M.G., Brown, N.W., Roberts, E.P.L.: The combination of adsorbent slurry sorption with adsorbent electrochemical regeneration for VOC removal. Chem. Eng. J. **198**, 130–137 (2012b)

Conti-Ramsden, M.G., Brown, N.W., Roberts, E.P.L.: Towards an odour control system combining slurry sorption and electrochemical regeneration. Chem. Eng. Sci. **79**, 219–227 (2012c)

Coughlin, R.W., Ezra, F.S., Tan, R.N.: Influence of chemisorbed oxgyen on adsorption onto carbon from aqueous solution. J. Colloid Interface Sci. **28**(4), 286–396 (1968)

Dreyer, D.R., Jia, H.P., Bielawski, C.W.: Graphene oxide: a convenient carbocatalyst for facilitating oxidation and hydration reactions. Angew Chem. Int. Ed. **49**, 6813–6816 (2010a)

Dreyer, D.R., Park, S., Bielawski, C.W., Ruoff, R.S.: The chemistry of graphene oxide. Chem. Soc. Rev. **39**(1), 228–240, doi: 10.1039/b917103g (2010b)

Dreyer, D.R., Jia, H.P., Todd, A.D., Geng, J., Bielawski, C.W.: Graphite oxide: A selective and highly efficient oxidant of thiols and sulfides. Org. Biomol. Chem. **9**(21), 7292–7295. doi: 10.1039/c1ob06102j (2011)

Garcia-Oton, M., Montilla, F., Lillo-Rodenas, M.A., Morallon, E., Vazquez, J.L.: Electrochemical regeneration of activated carbon saturated with toluene. J. Appl. Electrochem. **35**, 319–325 (2005)

Herold, A., Petitjean, D., Furdin, G., Klatt, M.: Exfoliation of graphite intercalation compounds—classification and discussion of the process from new experimental data relative to graphite-acid compounds. Mat. Sci. Forum. **152**, 281–288 (1994)

Ishikawa, T., Kanemaru, T., Teranishi, H., Onishi, K.: Composites of oxidized graphite material and expanded graphite material. United States Patent: 4,094,951 (1978)

Ishizaki, C., Cookson, J. John, T.: Adsorption of sulfur-containing taste and odor compounds. J. Water Pollut. Control Fed. **45**(3), 515–522 (1973)

Jia, H.P., Dreyer, D.R., Bielawski, C.W.: Graphite oxide as an auto-tandem oxidation-hydration-aldol coupling catalyst. Adv. Synth. Catal. **353**, 528–532 (2011)

Katoh, H., Kuniyoshi, I., Hirai, M., Shoda, M.: Studies of the oxidation mechanism of sulphur-containing gases on wet activated carbon fibre. Appl. Catal. **6**, 255–262 (1995)

Meeyoo, V., Trimm, D.L.: Adsorption-reaction processes for the removal of hydrogen sulphide from gas streams. J. Chem. Technol. Biotechnol. **68**, 411–416 (1997)

Mohammed, F.M., Roberts, E.P.L., Hill, A., Campen, A.K., Brown, N.W.: Continuous water treatment by adsorption and electrochemical regeneration. Water Res. **45**, 3065–3074 (2011)

Moreno-Castilla, C.: Adsorption of organic molecules from aqueous solutions on carbon materials. Carbon Balance Manage. **42**, 83–94 (2004)

Rafson, H.J.: Odour and VOC Control Handbook. McGraw-Hill, New York(1998)

Rios, R.V., Silvestre-Albero, J., Sepulveda-Escribano, A., Rodriguez-Reinoso, F.: Liquid phase removal of propanethiol by activated carbon: effect of porosity and functionality. Colloids Surf. A. **300**(12), 180–190 (2007)

Rios, R.V., Silvestre-Albero, J., Sepulveda-Escribano, A., Rodriguez-Reinoso, F.: Adsorption/oxidation of sulfur-containing species by activated carbon. NATO Sci. Peace Secur. 107–118 (2008)

Smet, E., Langenhove, H.V.: Abatement of volatile organic sulfur compounds in odorous emissions from the bio-industry. Biodegradation **9**, 271–284 (1998)

Yaws, C.L.: Yaws' Critical Property Data for Chemical Engineers and Chemists. Knovel (2012)

Zhou, M., Wang, Y., Zhai, Y., Zhai, J., Ren, W., Wang, F., Dong, S.: Controlled synthesis of large-area and patterned electrochemically reduced graphene oxide films. Chemistry **15**(25), 6116–6120, doi:10.1002/chem.200900596 (2009)