Combining adsorption with anodic oxidation as an innovative technique for removal and destruction of organics
N. W. Brown and E. P. L. Roberts

ABSTRACT
Coupling of adsorption with electrochemical oxidation is a novel approach to the treatment of aqueous organics that has demonstrated a number of key benefits over the individual application of these processes. This is based on a highly conducting adsorbent material, developed under the trade name Nyex™, that is able to rapidly adsorb the organics and anodically oxidise them within a single treatment unit. Successful scale up of the process (in both continuous and batch operation) has been achieved for the polishing of two separate groundwaters (one containing relatively simple petrol, diesel and their degradation products and the other with a range of more complex organics). Treatment showed that low discharge consents can be achieved, including the removal of more complex and difficult to treat compounds to below the limits of detection. Energy consumption for electrochemical regeneration was relatively low (down to 0.5 kWh/m³) suggesting that the process could be a practical alternative approach for effluent polishing.

Key words | adsorption, anodic oxidation, Arvia, groundwater, Nyex™

INTRODUCTION
Industrial activities on sites often results in contamination of the ground and groundwater, often with a range of toxic organic chemicals. One technique that is widely used is to pump the groundwater to the surface for treatment using one of a number of available remediation techniques. Whatever techniques are used, final effluent polishing is often achieved by adsorption onto granular activated carbon (GAC).

Adsorption using GAC is a widely used process for the removal of aqueous organic contaminants as very low discharge consents can be achieved (McKay 1996). However, adsorption is only a concentration process and after loading the GAC must either be disposed of (by landfill or incineration) or regenerated. Whilst thermal regeneration is the most widely-used process, it is a high energy, high-cost process with material loss rates of 5–10% requiring off-site transportation to specialist regenerators (McKay 1996). This has led to interest in alternative regeneration methods including solvent (Leng & Pinto 1996), ultrasonic (Zhang et al. 2003) and electrochemical (Narbaitz & Cen 1994), although these have not led to widespread industrial applications. Direct oxidation of the aqueous organics using electrochemical processes has been extensively investigated as it achieves destruction of the organics. However, the low conductivity of many wastewaters results in high cell voltages and treating low concentrations is limited due to mass transport of the organics to the electrodes (Murphy et al. 1995; Wang 2003).

An alternative approach developed at the University of Manchester, UK, combines the benefits of adsorption with electrochemical regeneration of the adsorbent via anodic oxidation (Brown et al. 2004; Brown & Roberts 2007). This is achieved by using a non-porous, highly conducting, carbon-based material, Nyex™. Adsorption achieves the concentration of the organics (eliminating mass transport during oxidation) and low discharge consents with electrochemical organics destruction at low cell voltages due to high conductivity of the Nyex. Previous studies on the process have shown that the system can be used to treat a wide range of organic concentrations from the treatment...
of neat oil in the nuclear industry (achieved by the addition of water and an emulsifying agent to create an aqueous waste) (Brown et al. 2013) to the removal of atrazine to below 0.5 ppb (Brown et al. 2004). This paper reports the scale up of the process to pilot plant level for the treatment of two groundwaters.

METHODS

Two groundwaters were investigated, one a mixture of complex organics from an agrochemical research centre (ARC) and the second from a petrol station (PS) redevelopment containing a mix of petrol, diesel and their degradation products. Both systems involved pump and treat. In the case of the ARC, there was an existing on-site treatment plant (40 m$^3$/hr) comprising balancing, air stripping, biological treatment (using filter beds) with GAC used for final effluent polishing. Remediation at the PS was air stripping and oil/water separation followed by GAC polishing.

The installed pilot plants were installed alongside the GAC plant and treated water was returned to the head of the works. The adsorbent material used in this work was supplied by Arvia Technology Ltd as a wet slurry containing approximately 50% dry Nyex 1000 in water. Nyex is based on a graphite intercalation compound, comprising particles with an average diameter of 500 nm. The material is non-porous (demonstrated by mercury porosimetry) and has a density 2.2 g/cm$^3$ (Mohammed et al. 2011), with a specific surface area of 0.79 m$^2$/g (measured by the Brunauer–Emmett–Teller (BET) method).

Whilst a number of priority pollutants had been identified at the ARC site, it was found during the period of operation that only a few were detectable within the influent to the pilot unit (see Table 1) (at concentrations ranging from 0.2 to 16 μg/l).

Laboratory scale

Initial treatment was undertaken in the laboratory using a batch treatment system as shown in Figure 1. This treatment was intended to show that the effluents could be successfully treated and no attempt was made to optimise treatment. It involved placing the sample of groundwater into the batch system and running a number of adsorption/regeneration cycles on the same adsorbate until chemical oxygen demand (COD) analysis had shown full removal of the organics. Table 2 gives the operating parameters used to treat the groundwaters from the two sites. Note that the samples used for laboratory treatment were taken several weeks before the pilot units were sent to site.

Pilot scale

On-site treatment used a continuous operation (Figure 1). This involved a three-stage process of adsorption, separation and regeneration, with all three stages being achieved within single process units. Both systems were in containerised units. Further details of the principles of operation for batch and continuous processes are given in Mohammed et al. (2011) and Brown et al. (2013).

Table 1 Level of priority pollutants in influent and effluent at different regeneration currents at a flow rate of 5 l/hr using Gemini reactor. All units in μg/l. Similar results obtained for batch reactor

<table>
<thead>
<tr>
<th>Determinant</th>
<th>Current 1A</th>
<th>Current 2A</th>
<th>Current 4A</th>
<th>Current 5A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Influent</td>
<td>Effluent</td>
<td>Influent</td>
<td>Effluent</td>
</tr>
<tr>
<td>Dimefox</td>
<td>0.1</td>
<td>&lt; 0.1</td>
<td>0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Ethofumesate</td>
<td>0.3</td>
<td>&lt; 0.1</td>
<td>0.4</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Hempa</td>
<td>9.2</td>
<td>&lt; 0.1</td>
<td>8.4</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Schradan</td>
<td>5.1</td>
<td>&lt; 0.1</td>
<td>4.3</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Simazine</td>
<td>0.3</td>
<td>1.1$^a$</td>
<td>0.3</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Dichlorprop</td>
<td>0.4</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Mecoprop</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>PAAH</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

$^a$This result is being treated as erroneous as it is higher than the influent levels in all samples analysed.
The pilot-scale sequential batch reactor (SBR) contained six electrochemical cells (50 cm × 50 cm), containing approximately 4 kg of Nyex, which created a bed between the membrane and the anode 22 mm deep. The cells contained graphite bi-polar flat sheet electrodes with a Daramic 350 membrane between the Nyex bed and the cathode. A 0.3% NaCl catholyte solution was pumped between the cathode and the membrane. The capacity of the system was 60 l/cycle.

The continuous (Gemini) reactor contained a single electrochemical cell with graphite electrodes 5 cm × 60 cm and the system contained approximately 2.5 kg of Nyex, giving a bed 22 mm deep. A Daraminc membrane and 0.3% NaCl catholyte were again used. The Gemini was only used to treat the ARC groundwater. Varying flow rates (5–30 l/hr) and currents (1–5 A) were investigated. Hydrogen gas generated at the cathode was removed via local exhaust ventilation either via a hood over the SBR or through an extractor fan in the container.

Adsorption was achieved in both cases by mixing the adsorbent with the water to be treated using compressed air. Sedimentation was achieved in batch operation by switching off the air and allowing the adsorbent to settle into electrochemical cells at the bottom of the tank. In the continuous process this was achieved by the adsorbent/water mixture flowing into the middle section where no air was present allowing the adsorbent to settle to create a moving bed which passed between two electrodes. Electrochemical regeneration was achieved by passing direct electric current through the cells. In these trials treatment was achieved using one adsorption/regeneration cycle and then the treated groundwater was discharged and fresh effluent added.

**Analysis**

COD was determined using Hach COD tubes (0–150 mg/l) and a Hach colorimeter (DR890). Priority pollutants in the ARC effluent were determined by gas chromatography–mass spectrometry at an independent laboratory (SAL – Manchester, UK). Monitoring of the off-gases was undertaken during operation of the Gemini and SBR systems whilst treating the ARC groundwaters. This was undertaken by Envirocare Ltd (a consultancy specialising in gas monitoring) to assess the potential health, safety and environmental impacts. The ARC groundwater was chosen as there was a
wide range of pollutants in the effluent, and site treatment involved both continuous and batch treatment.

The current efficiency (CE) was calculated using

\[
CE = \frac{(COD_i - COD_o)V F}{8 i t}
\]

where \(COD_i\) and \(COD_o\) are the initial (or inlet) and final (or outlet) CODs (g/l), \(V\) is the volume treated or passed through the cell (l), \(i\) is the cell current (A), \(t\) is the treatment time (s) and \(F\) is the Faraday constant (96,487 C/g). Since the main use of energy within the process is typically the energy for electrochemical regeneration, the energy requirement is based on regeneration energy in kWh/m³.

**RESULTS**

Small-scale treatment of the groundwaters in the laboratory was undertaken, which showed that both effluents could be successfully treated (Figure 2). Whilst these trials were not optimised they provided initial conditions for the site pilot SBR trials. They gave regeneration energies of 1.8 and 2.8 kWh/m³ for the ARC and PS effluent, respectively, with charges passed of 75 and 55 C/mg COD removed, and current efficiencies of 16 and 22%.

Figure 3 shows the performance of the pilot-scale SBR over a range of operating conditions for the PS and ARC over a range of operating conditions.

With the data from the PS it is clear that a regeneration energy of 0.5 kWh/m³ (50 kWh/kg COD removed) achieves
full recovery of the adsorbent capacity. This equates to a charge passed of 50–60 C/mg COD, giving typical current efficiencies of 20%. However, the higher organic loads in the ARC groundwater require higher energies to achieve full recovery of the adsorbent capacity. In this trial when the groundwater has an incoming COD of around 20 mg/l, then a regeneration energy of around 1.1 kWh/m³ (55 kWh/kg COD removed) is sufficient, but at 0.65 kWh/m³, there is insufficient recovery and the performance of the system drops off. This gives a charge passed of around 70–80 C/mg COD removed with typical current efficiencies of 15%. Whilst these are in-line with the results obtained from the laboratory-scale work (allowing for the variation on the incoming COD), they give regeneration energies higher than obtained in other tests, for example 14.2 kWh/kg COD removed for the destruction of radioactive oils (Brown et al. 2013) and 6.6–22 kWh/kg COD removed for the treatment of crystal violet and phenol in deionised water (Brown 2005). This is believed to be due to poor mixing within the larger electrochemical cells and a need for further optimisation.

A series of the regenerations on the ARC groundwater were undertaken by holding the current at 10 A and varying the regeneration time to get different regeneration energies (Figure 4). This demonstrates the effect of increasing regeneration time (and also energy) on the removal of COD.

Whilst previous research has demonstrated a small increase in performance at warm temperatures (unpublished data), the field trial on the PS groundwater also showed good performance even at the low water temperatures experienced at the site (<5 °C).

The results from the continuous Gemini system are shown in Figure 5, where the average COD removal for a range of energy inputs is shown. In this figure the data at the higher flow rates have been eliminated as at higher flow rates (>15 l/hr) the COD removal in the system was very low, whatever current was applied. This suggests that at these flow rates, the system was limited by the adsorption that could be achieved. Even 15 l/hr is believed to make the system adsorption limited as decreasing the flow rate of the Gemini system from 15 to 5 l/hr, but keeping the regeneration energy at 1.4 kWh/m³, increased the COD removal rate from 28 to 100%. Hence, the adsorptive loading of the Nyex must be considered in the design of the treatment unit.

If only the data for flows of 5 l/hr are considered then there is a very clear relationship between the applied current and the outlet COD achieved. These trials clearly demonstrate that under the same adsorption conditions, the regeneration current can control the degree of treatment.
required. It demonstrates the system has the ability to control the degree of treatment that the groundwater receives. This controllability is a significant benefit of the Arvia™ Process.

Comparable results were achieved at pilot scale using both continuous (1.6 kWh/m³ and 66 C/mg COD) and batch (1.1 kWh/m³ and 54 C/mg COD) treatment.

**Priority pollutants**

As well as assessing the removal of organics as measured by COD, the removal of specific priority pollutants was investigated to see if these would be preferentially removed during treatment (Table 1). All were removed to below the detection limit of 0.1 or 0.2 μg/l (with the exception of Dicamba) even when the applied regeneration energy was low and there was low removal of organics as measured by COD. This suggests that there is preferential removal of pesticides. This preferential removal of certain organics has previously been reported (Brown & Roberts 2007).

However, it also highlighted that limited removal of Dicamba is occurring. This is believed to be due to its solubility, which means that it preferentially remains in the aqueous phase rather than adsorbing onto the Nyex particles. Activated carbon is also likely to find this specific compound difficult to remove as well (Yelverton et al. 1992), possibly due to its high solubility.

**Gaseous emissions**

The environmental impacts from the Arvia™ Process are low (Ropka 2010) as the system does not produce any secondary waste streams other than waste gases. Analysis of these gases showed that there were low quantities of carbon dioxide, hydrogen, carbon monoxide and chlorine in the off-gases. Hydrogen is generated at the cathode and the other gases at the anode and these are all discharged to atmosphere. Their independent report concluded that:

‘although there is a certain degree of detection of the pollutants in question, their levels are generally extremely low’.

Off-gas removal via local exhaust ventilation without any further treatment should be possible.

**Comparative energy consumption**

These trials show energy levels towards the lower end of those reported in the literature. Canizares et al. (2004) reported 84.03 kWh/kg COD for 80% electrochemical regeneration of activated carbon loaded with phenol. For direct electrochemical oxidation, values range from 12.9 to 73.4 kWh/kg COD for the removal of COD from domestic wastewater at Ti/Pt anode (Vlyssides et al. 2002), 30-50 kWh/kg COD at highly doped SnO2 anodes (Stucki et al. 1994) and 32.4 kWh/kg COD for biologically treated industrial effluent (Roosens et al. 2004).

Accounting for the adsorptive capacity achieved in this work should allow the charge passed to be reduced, reducing the energy for regeneration. The data show that the adsorptive capacity of the Nyex must be considered the limiting factor when treating the low concentrations of organics that can often occur in groundwater situations.

**DISCUSSION**

This trial highlighted the benefits of on-site treatment with no need to transport waste materials off-site. However operational performance of the plant should also be considered.

**Nyex lifetime**

Whilst each unit was filled with fresh Nyex at the start of the on-site work, this was regenerated and reused so that the same Nyex was used for all experiments in that unit. Obviously, the approach used by this process relies on the Nyex being fully regenerated with no loss of adsorbent as otherwise the rapid recycling of adsorbent through the process would rapidly reduce its performance. Whilst not specifically tested in this work, other studies (Brown 2005) have shown that the Nyex can be recycled many times with no noticeable loss in adsorptive capacity. This suggests that the Nyex can be used many times and no lifetime has yet been observed, although it is anticipated that a small make up of Nyex may be required as there is likely to be some adsorbent carryover.

**CONCLUSIONS**

This project has shown that the scaled up process is effective in treating groundwater containing both ‘simple’ and ‘complex’ organics to a standard where it could be disposed of via the site’s existing discharge consents. The results suggest that the process has merit in the on-site treatment of groundwater. The regeneration energy used for treatment in these
studies was found to be 1.1 and 0.5 kWh/m³ for the ARC and PS groundwaters, respectively, with similar results being obtained for batch and continuous treatment. The charge passed to achieve the regeneration was greater than anticipated and suggested that there is room for optimisation. The work demonstrated that the adsorptive capacity of the Nyex must be considered as the limiting factor when treating the low concentrations of organics that can often occur in groundwater.

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REFERENCES


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